Supporting Information

Additive-free coupling of bromoalkynes with secondary phosphine oxides to generate alkynylphosphine oxides in acetic anhydride

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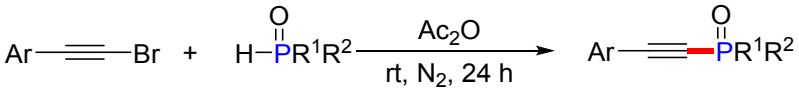
1. General remarks

All reactions were conducted in clean glassware with magnetic stirring. Chromatographic purification was performed on silica gel (400~500 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao), which was detected by fluorescence. ^{1}H NMR (400 MHz or 600 MHz), ^{13}C NMR (100 MHz or 150 MHz) and ^{31}P NMR (162 MHz or 243 HMz) spectra were measured with a Bruker AC 400 spectrometer or Bruker Avance Neo 600 spectrometer with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

2. General procedure for the synthesis of alkynylphosphine oxide

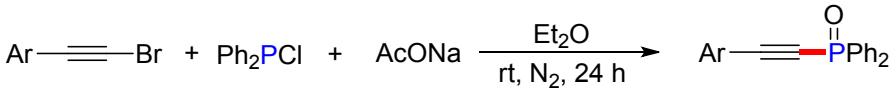


To a solution of secondary phosphine oxide (0.60 mmol) in 1.0 mL of acetic anhydride was added bromoalkyne (0.20 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 24 h at room temperature. The residue was then purified by column chromatography on silica gel (petroleum ether/AcOEt 1:1) to give the pure product.

The preparation of diphenyl(phenylethynyl)phosphine oxide (3aa) in 4.0 mmol scale

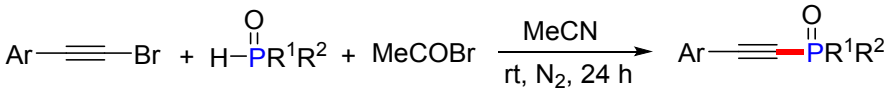
Diphenylphosphine oxide (2.43 g, 12.0 mmol) and bromoalkyne (720 mg, 4.0 mmol) were added in acetic anhydride (15 mL) under nitrogen atmosphere, and the reaction mixture was stirred room temperature for 24 h. The residue was then purified by silica gel column chromatography (petroleum ether/EtOAc = 1:1) to give pure product compound **3aa** (846 mg, 70% yield). If the reaction was accomplished in 2.0 mmol scale, the desired compound **3aa** was obtained in 83% yield.

3. The reaction of bromoalkyne, Ph_2PCl and AcONa



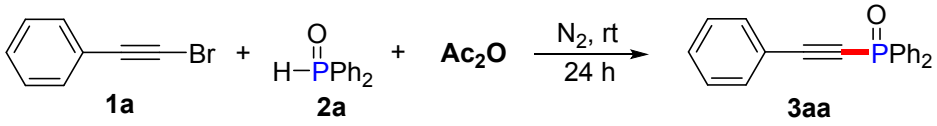
To a solution of chlorodiphenylphosphine (0.60 mmol) in 2 mL of ether was added sodium acetate (0.60 mmol) and bromoalkyne (0.20 mmol) under nitrogen atmosphere. Then the reaction mixture was stirred for 24 h at room temperature. The residue was then purified by column chromatography on silica gel (petroleum ether/AcOEt 1:1) to give the pure product.

4. The reaction of bromoalkyne, $HP(O)R^1R^2$ and MeCOBr



To a solution of secondary phosphine oxide (0.60 mmol) in 2 mL of acetonitrile was added bromoalkyne (0.20 mmol) and acetyl bromide (0.60 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 24 h at room temperature. The residue was then purified by column chromatography on silica gel (petroleum ether/AcOEt 1:1) to give the pure product.

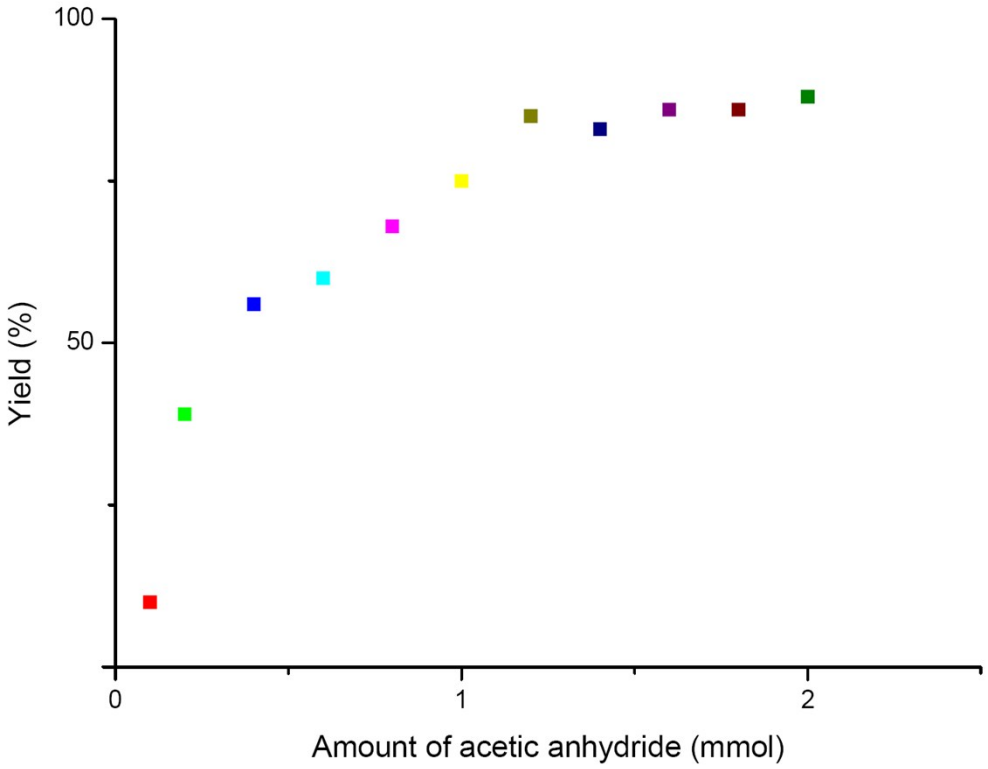
5. The effect of the amount of acetic anhydride on the yield of 3aa



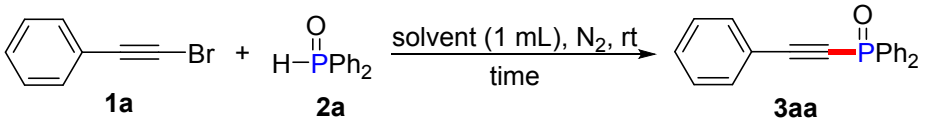
1a 2a 3aa

Entry	Ac_2O	Yield[a] (%)
1	0.10 mmol	10
2	0.20 mmol	39
3	0.40 mmol	56
4	0.60 mmol	60
5	0.80 mmol	68
6	1.0 mmol	75
7	1.2 mmol	85
8	1.4 mmol	83
9	1.6 mmol	86
10	1.8 mmol	86
11	2.0 mmol	88

[a] Isolated yield.



6. The effect of reaction time and solvent on the yield of 3aa



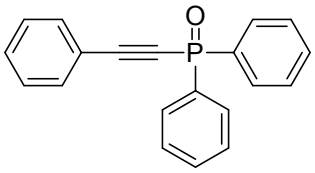
1a 2a 3aa

Entry	time	solvent	Yield[a] (%)
1	1 h	Ac_2O	35[b]
2	3 h	Ac_2O	55[b]
3	6 h	Ac_2O	66[b]
4	12 h	Ac_2O	78[b]
5	24 h	Ac_2O	92[b]
6	36 h	Ac_2O	91[b]
7	24 h	acetone	< 10[c]
8	24 h	THF	20[c]
9	24 h	CH_3CN	62[c]
10	24 h	CH_2Cl_2	81[c]

[a] Isolated yield. [b] Reaction conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), Ac_2O (1.0 mL) at room temperature under a N_2 atmosphere.[c] Reaction conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), Ac_2O (0.60 mmol), solvent (1 mL) at room temperature under a N_2 atmosphere.

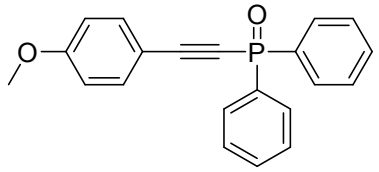
7. Characterization Data for All Products

Diphenyl(phenylethynyl)phosphine oxide (3aa)[1]



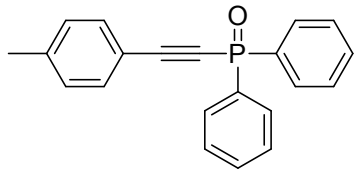
White solid (55 mg, 92% yield). Mp: 101–102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.88 (m, 4H), 7.60–7.43 (m, 9H), 7.39–7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6 (d, J = 121.4 Hz), 132.5 (d, J = 1.7 Hz), 132.2 (d, J = 2.8 Hz), 131.0 (d, J = 11.2 Hz), 130.7, 128.7, 128.5, 119.9 (d, J = 3.9 Hz), 105.5 (d, J = 29.7 Hz), 83.7 (d, J = 168.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.31.

((4-Methoxyphenyl)ethynyl)diphenylphosphine oxide (3ba)[2]



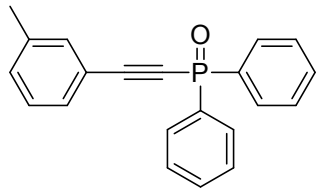
Colorless oil (60 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.88 (dd, *J* = 13.8, 7.8 Hz, 4H), 7.54–7.46 (m, 8H), 6.88–6.87 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.4, 134.3, 133.7 (d, *J* = 121.4 Hz), 132.1 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 11.0 Hz), 128.6 (d, *J* = 13.2 Hz), 114.2, 111.7 (d, *J* = 4.1 Hz), 106.2 (d, *J* = 30.9 Hz), 82.3 (d, *J* = 171.9 Hz), 55.4. ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.18.

Diphenyl(p-tolylethynyl)phosphine oxide (3ca)[1]



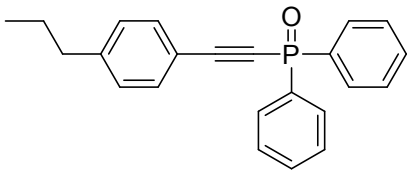
White solid (56 mg, 88% yield). Mp: 162–164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.87 (m, 4H), 7.56–7.46 (m, 8H), 7.19–7.17 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 132.7 (d, *J* = 121.4 Hz), 131.4 (d, *J* = 1.8 Hz), 131.1 (d, *J* = 2.8 Hz), 129.9 (d, *J* = 11.1 Hz), 128.3, 127.6 (d, *J* = 13.4 Hz), 115.8 (d, *J* = 4.1 Hz), 105.1 (d, *J* = 30.3 Hz), 82.0 (d, *J* = 170.6 Hz), 20.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.32.

Diphenyl(m-tolylethynyl)phosphine oxide (3da)[1]



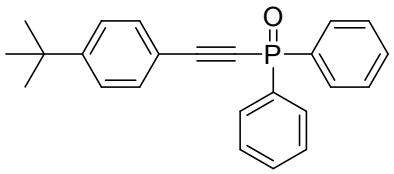
White solid (56 mg, 89% yield). Mp: 155–156 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.87 (m, 4H), 7.56–7.46 (m, 6H), 7.41–7.39 (m, 2H), 7.26–7.25 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 133.7 (d, *J* = 121.3 Hz), 132.9 (d, *J* = 1.9 Hz), 132.2 (d, *J* = 2.8 Hz), 131.6, 131.0 (d, *J* = 11.1 Hz), 129.6 (d, *J* = 1.9 Hz), 128.7 (d, *J* = 13.3 Hz), 128.4, 119.7 (d, *J* = 4.2 Hz), 105.9 (d, *J* = 29.9 Hz), 83.3 (d, *J* = 169.7 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.25.

Diphenyl((4-propylphenyl)ethynyl)phosphine oxide (3ea)



Yellow soild (59 mg, 86% yield). Mp: 100–101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.87 (m, 4H), 7.56–7.46 (m, 8H), 7.19–7.17 (d, *J* = 8.4 Hz, 2H), 2.62–2.58 (t, *J* = 7.2 Hz, 2H), 1.68–1.58 (m, 2H), 0.94–0.91 (t, *J*= 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 133.9 (d, *J* = 121.3 Hz), 132.5 (d, *J* = 1.8 Hz), 132.1 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 11.1 Hz), 128.7 (d, *J* = 7.2 Hz), 128.5, 117.1, 106.1 (d, *J* = 30.2 Hz), 83.1 (d, *J* = 170.3 Hz), 38.0, 24.1, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.25. HRMS (ESI) calcd for $C_{23}H_{21}OP$ $(M+H)^+$: 345.14028; Found: 345.14059.

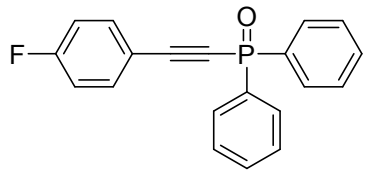
((4-(*tert*-Butyl)phenyl)ethynyl)diphenylphosphine oxide (3fa)[2]



Colorless oil (55 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.87 (dd, *J* = 14.0, 7.2 Hz, 4H), 7.55–7.48 (m, 8H), 7.41–7.38 (d, *J* = 8.4 Hz,, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 133.7 (d, *J* = 121.6 Hz), 132.4 (d, *J* = 1.7

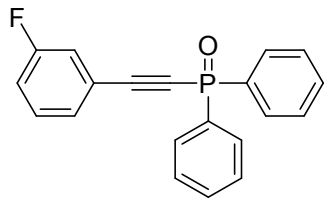
Hz), 132.2 (d, J = 2.7 Hz), 131.0 (d, J = 11.2 Hz), 128.7 (d, J = 13.4 Hz), 125.6, 116.8 (d, J = 4.0 Hz), 106.2 (d, J = 30.3 Hz), 83.0 (d, J = 171.0 Hz), 35.0, 31.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.49.

((4-Fluorophenyl)ethynyl)diphenylphosphine oxide (3ga)[1]



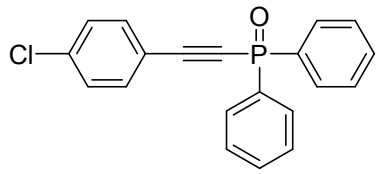
White solid (54 mg, 85% yield). Mp: 121–123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.87 (m, 4H), 7.61–7.54 (m, 4H), 7.52–7.47 (m, 4H), 7.10–7.05 (t, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (d, J = 252.1 Hz), 134.8 (dd, J = 8.8, 1.8 Hz), 133.5, 132.3, 132.3, 131.0 (d, J = 11.1 Hz), 128.7 (d, J = 13.4 Hz), 116.2 (d, J = 22.2 Hz), 104.4 (d, J = 29.8 Hz), 83.7 (d, J = 167.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.30.

((3-Fluorophenyl)ethynyl)diphenylphosphine oxide (3ha)[3]



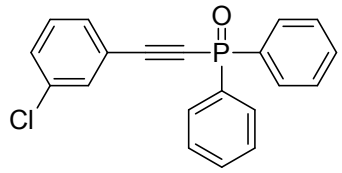
White solid (55 mg, 86% yield). Mp: 118–120 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.87 (dd, J = 13.8, 7.2 Hz, 4H), 7.57–7.55 (m, 2H), 7.51–7.48 (m, 4H), 7.39–7.33 (m, 2H), 7.29–7.21 (m, 1H), 7.17–7.14 (t, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.0 (d, J = 246.9 Hz), 133.1 (d, J = 121.5 Hz), 132.4 (d, J = 2.4 Hz), 131.0 (d, J = 11.1 Hz), 130.4 (d, J = 8.6 Hz), 128.7 (d, J = 13.4 Hz), 128.5, 121.7 (dd, J =8.9, 3.6 Hz), 119.3 (d, J = 24.2 Hz), 118.3 (d, J = 21.2 Hz), 103.6 (dd, J = 29.1, 3.0 Hz), 84.4 (d, J = 165.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.34.

((4-Chlorophenyl)ethynyl)diphenylphosphine oxide (3ia)[1]



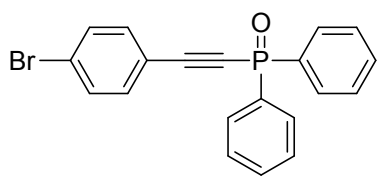
White soild (54 mg, 81% yield). Mp: 152–153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.58–7.47 (m, 8H), 7.36–7.34 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 132.7 (d, *J* = 1.8 Hz), 132.3 (d, *J* = 121.5 Hz), 131.3 (d, *J* = 2.8 Hz), 130.0 (d, *J* = 11.2 Hz), 128.0, 127.7 (d, *J* = 13.4 Hz), 117.4 (d, *J* = 4.0 Hz), 103.1 (d, *J* = 29.4 Hz), 83.8 (d, *J* = 166.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.36.

((3-Chlorophenyl)ethynyl)diphenylphosphine oxide (3ja)[1]



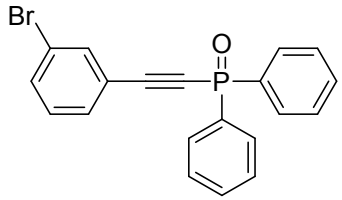
Yellow oil (50 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.59–7.55 (m, 3H), 7.52–7.47 (m, 5H), 7.44–7.41 (m, 1H), 7.34–7.30 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 134.5, 133.3 (d, *J* = 121.4 Hz), 132.4 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 2.0 Hz), 131.0 (d, *J* = 11.1 Hz), 131.0, 130.6 (d, *J* = 1.9 Hz), 129.9, 128.8 (d, *J* = 13.4 Hz), 121.6 (d, *J* = 4.0 Hz), 103.5 (d, *J* = 29.0 Hz), 85.0 (d, *J* = 165.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.33.

((4-Bromophenyl)ethynyl)diphenylphosphine oxide (3ka)[1]



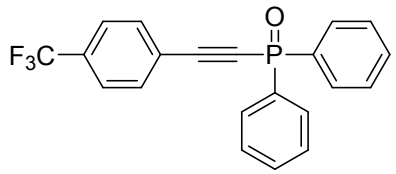
White solid (53 mg, 70% yield). Mp: 142–144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.58–7.44 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ. 133.8 (d, *J* = 1.8 Hz), 133.3 (d, *J* = 121.4 Hz), 132.4 (d, *J* = 2.9 Hz), 131.9, 131.0 (d, *J* = 11.2 Hz), 128.8 (d, *J* = 13.4 Hz), 125.5, 118.8 (d, *J* = 4.1 Hz), 104.2 (d, *J* = 29.5 Hz), 84.9 (d, *J* = 165.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.42.

((3-Bromophenyl)ethynyl)diphenylphosphine oxide (3la)[4]



White solid (62 mg, 80% yield). Mp: 106–107 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90–7.87 (dd, *J* = 13.8, 7.2 Hz, 4H), 7.72 (s, 1H), 7.57–7.55 (m, 3H), 7.52–7.48 (m, 5H), 7.27–7.23 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.0 (d, *J* = 1.7 Hz), 133.9, 133.0 (d, *J* = 121.4 Hz), 132.4 (d, *J* = 2.4 Hz), 131.1, 131.0 (d, *J* = 10.5 Hz), 130.1, 128.8 (d, *J* = 13.2 Hz), 122.3, 121.9 (d, *J* = 3.9 Hz), 103.3 (d, *J* = 29.3 Hz), 84.8 (d, *J* = 164.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.31.

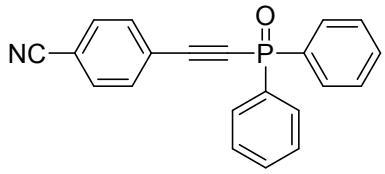
Diphenyl((4-(trifluoromethyl)phenyl)ethynyl)phosphine oxide (3ma)[5]



White solid (60 mg, 81% yield). Mp: 158–159 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.88 (dd, *J* = 13.8, 7.2 Hz, 4H), 7.72–7.70 (d, *J* = 7.8 Hz, 2H), 7.65–7.64 (d, *J* = 8.4 Hz, 2H), 7.59–7.57 (m, 2H), 7.53–7.50 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.9 (d, *J* = 121.5 Hz), 132.8 (d, *J* = 1.7 Hz), 132.5 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 33.0 Hz), 131.0 (d, *J* = 11.1 Hz), 128.8 (d, *J* = 13.4 Hz), 125.5 (q, *J* =

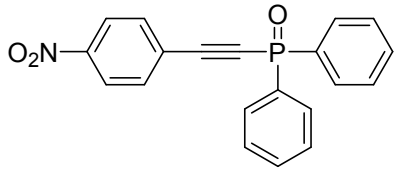
3.5 Hz), 123.7, 122.5, 103.2 (d, J = 28.8 Hz), 85.8 (d, J = 163.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.40.

4-((Diphenylphosphoryl)ethynyl)benzonitrile (3na)[2]



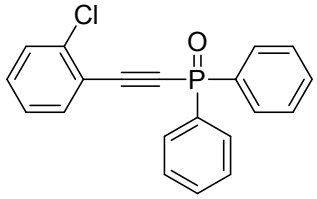
White solid (55 mg, 84% yield). Mp: 101–102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.85 (m, 4H), 7.70–7.66 (m, 4H), 7.61–7.57 (m, 2H), 7.54–7.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0 (d, J = 1.8 Hz), 132.9 (d, J = 121.8 Hz), 132.6 (d, J = 2.8 Hz), 132.2, 131.0 (d, J = 11.2 Hz), 128.8 (d, J = 13.5 Hz), 124.6 (d, J = 3.8Hz), 117.7, 114.1, 102.4 (d, J = 28.0 Hz), 87.8 (d, J = 160.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.46.

((4-Nitrophenyl)ethynyl)diphenylphosphine oxide (3oa)[2]



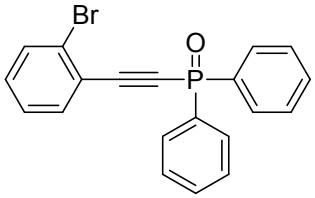
Yellow soild (44 mg, 64% yield). Mp: 165–167 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26–8.23 (d, J = 8.4 Hz, 2H), 7.92–7.87 (m, 4H), 7.77–7.75 (d, J = 8.8 Hz, 2H), 7.61–7.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 133.4 (d, J = 1.6 Hz), 132.7 (d, J = 121.6 Hz), 132.6 (d, J = 2.8 Hz), 131.0 (d, J = 11.2 Hz), 128.9 (d, J = 13.5 Hz), 126.4 (d, J = 4.0 Hz), 123.7, 102.1 (d, J = 28.1 Hz), 88.4 (d, J = 159.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.64.

((2-Chlorophenyl)ethynyl)diphenylphosphine oxide (3qa)[1]



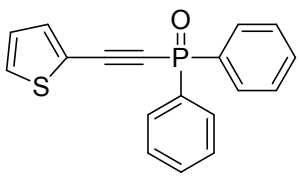
Yellow oil (54 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.92 (m, 4H), 7.62–7.60 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.57–7.43 (m, 7H), 7.39–7.35 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29–7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1 (d, *J* = 2.1 Hz), 134.3 (d, *J* = 1.9 Hz), 133.4 (d, *J* = 121.4 Hz), 132.3 (d, *J* = 2.9 Hz), 131.6, 131.1 (d, *J* = 10.2 Hz), 129.5, 128.7 (d, *J* = 13.5 Hz), 126.7, 120.3 (d, *J* = 4.0 Hz), 101.5 (d, *J* = 29.5 Hz), 88.6 (d, *J* =165.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.59.

((2-Bromophenyl)ethynyl)diphenylphosphine oxide (3ra)



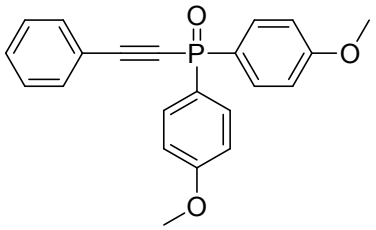
Colorless oil (55 mg, 73% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–7.94 (dd, *J* = 13.8, 1.8 Hz, 4H), 7.63–7.60 (m, 2H), 7.57–7.54 (m, 2H), 7.51–7.48 (m, 4H), 7.33–7.28 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 134.5 (d, *J* = 1.4 Hz), 133.2 (d, *J* = 121.7 Hz), 132.7, 132.3 (d, *J* = 2.7 Hz), 131.7, 131.1 (d, *J* = 11.1 Hz), 128.7 (d, *J* = 13.5 Hz), 127.3, 126.2 (d, *J* = 1.7 Hz), 122.5 (d, *J* = 3.6 Hz), 103.0 (d, *J* = 29.3 Hz), 87.6 (d, *J* = 165.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.58. HRMS (ESI) calcd for $C_{20}H_{14}BrOP$ $(M+H)^+$: 381.00384; Found: 381.00397.

Diphenyl(thiophen-2-ylethynyl)phosphine oxide (3sa)[1]



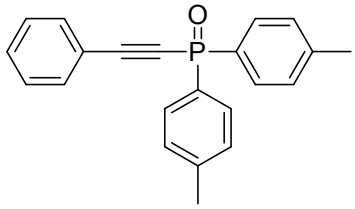
Yellow oil (41mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.56–7.54 (m, 2H), 7.50–7.46 (m, 5H), 7.43–7.42 (m, 1H), 7.04–7.02 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.8 (d, *J* = 1.7 Hz), 133.2 (d, *J* = 122.0 Hz), 132.3 (d, *J* = 2.4 Hz), 131.0 (d, *J* = 11.1 Hz), 130.6, 128.7 (d, *J* = 13.8 Hz), 127.4, 119.6 (d, *J* = 4.4 Hz), 98.8 (d, *J* = 30.5 Hz), 87.4 (d, *J* = 167.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.39.

Bis(4-methoxyphenyl)(phenylethynyl)phosphine oxide (3ab)



Yellow oil (50 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.78 (dd, *J* = 13.2, 9.0 Hz, 4H), 7.58–7.57 (d, *J* = 7.2 Hz, 2H), 7.45–7.42 (m, 1H), 7.38–7.35 (m, 2H), 6.99–6.98 (dd, *J* = 8.4, 1.8 Hz, 4H), 3.85 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7 (d, *J* = 3.0 Hz), 132.9 (d, *J* = 12.6 Hz), 132.4, 130.5, 128.5, 125.0 (d, *J* = 128.3 Hz), 120.2 (d, *J* = 3.8 Hz), 114.2 (d, *J* = 14.4 Hz), 104.8 (d, *J* = 30.0 Hz), 84.1 (d, *J* = 167.7 Hz), 55.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.10. HRMS (ESI) calcd for $C_{22}H_{19}O_3P$ $(M+H)^+$: 363.11446; Found: 363.11487.

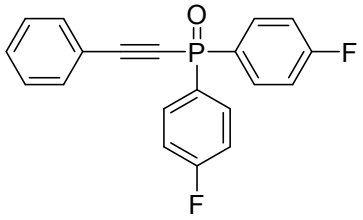
(Penylethynyl)di-p-tolylphosphine oxide (3ac)[3]



Colorless oil (52 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.75 (dd, *J*= 13.6, 8.0 Hz, 4H), 7.58–7.56 (m, 2H), 7.45–7.41 (m, 1H), 7.37–7.34 (m, 2H), 7.30–

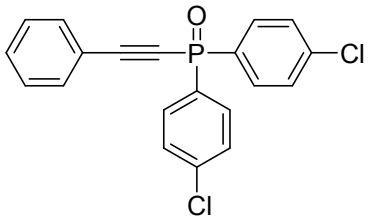
7.26 (m, 4H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7 (d, *J* = 2.8 Hz), 132.4 (d, *J* = 1.8 Hz), 131.0 (d, *J* = 11.5 Hz), 130.6, 130.5, 129.4 (d, *J* = 13.9 Hz), 128.5, 120.1 (d, *J* = 4.0 Hz), 105.0 (d, *J* = 29.6 Hz), 84.2 (d, *J* = 168.0 Hz), 21.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.67.

Bis(4-fluorophenyl)(phenylethynyl)phosphine oxide (3ad)[2]



Colorless oil (49 mg, 72% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.86 (m, 4H), 7.60–7.59 (m, 2H), 7.49–7.46 (m, 1H), 7.40–7.38 (m, 2H), 7.21–7.17 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2 (dd, *J* = 252.5, 3.2 Hz), 133.5 (dd, *J* = 12.9, 8.7 Hz), 132.5 (d, *J* = 1.8 Hz), 130.9, 129.3 (dd, *J* = 125.6, 3.2 Hz), 128.6, 119.6 (d, *J* = 4.1 Hz), 116.3 (dd, *J* = 21.6, 15.0 Hz), 106.1 (d, *J* = 30.8 Hz), 82.9 (d, *J* = 171.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 6.19.

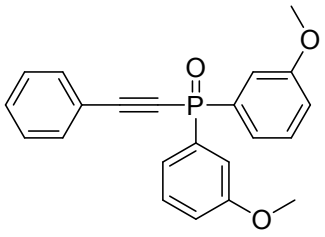
Bis(4-chlorophenyl)(phenylethynyl)phosphine oxide (3ae)[1]



Yellow oil (59 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83–7.80 (dd, *J* = 13.2 Hz, 8.4 Hz, 4H), 7.60–7.59 (d, *J* = 7.2 Hz, 2H), 7.49–7.46 (m, 5H), 7.40–7.38 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1 (d, *J* = 3.5 Hz), 132.6, 132.3 (d, *J* = 12.2 Hz), 131.6 (d, *J* = 123.8 Hz), 131.0, 129.2 (d, *J* = 14.1 Hz), 128.6, 119.4 (d, *J* = 3.9 Hz), 106.4 (d, *J* = 30.8 Hz), 82.6 (d, *J* = 173.3 Hz). ^{31}P NMR (243

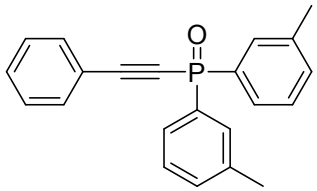
MHz, $CDCl_3$): δ 6.14.

Bis(3-methoxyphenyl)(phenylethynyl)phosphine oxide (3af)



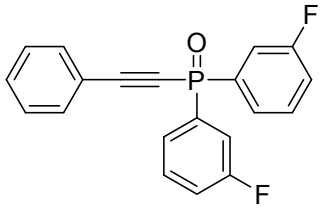
Colorless oil (44 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.58 (m, 2H), 7.47–7.35 (m, 9H), 7.09–7.06 (m, 2H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (d, *J* = 16.7 Hz), 134.8 (d, *J* = 120.9 Hz), 132.5 (d, *J* = 1.9 Hz), 130.7, 130.0 (d, *J* = 15.9 Hz), 128.5, 123.2 (d, *J* = 11.1 Hz), 119.9 (d, *J* = 4.0 Hz), 118.5 (d, *J* = 2.8 Hz), 115.7 (d, *J* = 12.3 Hz), 105.5 (d, *J* = 30.1 Hz), 83.6 (d, *J* = 170.0 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.38. HRMS (ESI) calcd for $C_{22}H_{19}O_3P$ $(M+H)^+$: 363.11446; Found: 363.11401.

(Phenylethynyl)di-m-tolylphosphine oxide (3ag)



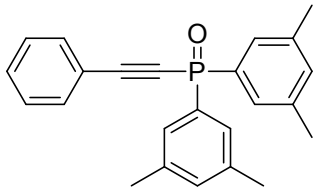
Colorless oil (45 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74–7.72 (d, *J* = 12 Hz, 2H), 7.69–7.65 (dd, *J* = 13.8, 7.2 Hz, 2H), 7.60–7.59 (m, 2H), 7.46–7.43 (m, 1H), 7.39–7.34 (m, 6H), 2.39 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.6 (d, *J* = 13.4 Hz), 133.3, 133.0 (d, *J* = 3.0 Hz), 132.5 (d, *J* = 1.8 Hz), 131.4 (d, *J* = 10.9 Hz), 130.6, 128.5, 128.4, 128.1 (d, *J* = 11.7 Hz), 120.1 (d, *J* = 3.6 Hz), 105.2 (d, *J* = 29.4 Hz), 83.7 (d, *J* = 167.7 Hz), 21.4. ^{31}P NMR (243 MHz, $CDCl_3$): δ 8.69. HRMS (ESI) calcd for $C_{22}H_{19}OP$ $(M+H)^+$: 331.12463; Found: 331.12497.

Bis(3-fluorophenyl)(phenylethynyl)phosphine oxide (3ah)



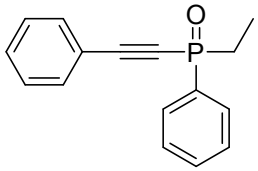
Colorless oil (41 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.66 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.63–7.56 (m, 4H), 7.54–7.47 (m, 3H), 7.42–7.39 (t, *J* = 7.6, 2H), 7.29–7.25 (t, *J*= 9.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9 (dd, *J* = 249.3, 19.0 Hz), 135.8 (dd, *J* = 121.9, 5.8 Hz), 132.6 (d, *J* = 1.8 Hz), 131.1, 130.9 (dd, *J* = 15.8, 7.5 Hz), 128.7, 126.7 (dd, *J* = 10.5, 3.3 Hz), 119.8 (dd, *J* = 21.2, 2.6 Hz), 119.4 (d, *J* = 4.1 Hz), 118.0 (dd, *J* = 22.6, 12.3 Hz), 106.6 (d, *J* = 31.2 Hz), 82.5 (d, *J* = 174.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 5.32. HRMS (ESI) calcd for $C_{20}H_{13}F_2OP$ $(M+H)^+$: 339.07448; Found: 339.07477.

Bis(3,5-dimethylphenyl)(phenylethynyl)phosphine oxide (3ai)[3]



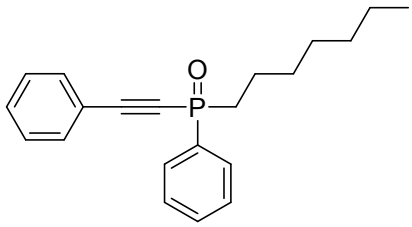
Colorless oil (54 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.58 (m, 2H), 7.52–7.48 (d, *J* = 14.0 Hz, 4H), 7.46–7.42 (m, 1H), 7.39–7.35 (m, 2H), 7.16 (s, 2H), 2.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4 (d, *J* = 14.0 Hz), 133.9 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 199.9 Hz), 132.5 (d, *J* = 1.8 Hz), 130.5, 128.5 (d, *J* = 2.7 Hz), 128.4, 120.2, 104.9 (d, *J* = 29.4 Hz), 84.2 (d, *J* = 168.4 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.12.

Ethyl(phenyl)(phenylethynyl)phosphine oxide (3aj)



Colorless oil (32 mg, 64% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93–7.89 (m, 2H), 7.58–7.57 (m, 3H), 7.54–7.51 (m, 2H), 7.46–7.43 (m, 1H), 7.39–7.36 (m, 2H), 2.18–2.12 (m, 2H), 1.28–1.22 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.5, 132.2 (d, *J* = 2.4 Hz), 132.1 (d, *J* = 114.5 Hz), 130.5 (d, *J* = 6.5 Hz), 130.4, 128.7 (d, *J* = 12.5 Hz), 128.5, 120.0 (d, *J* = 4.1 Hz), 104.0 (d, *J* = 27.3 Hz), 82.9 (d, *J* = 156.3 Hz), 27.2 (d, *J* = 84.5 Hz), 6.0 (d, *J* = 5.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 19.18. HRMS (ESI) calcd for $C_{16}H_{15}OP$ $(M+H)^+$: 255.09333; Found: 255.09349.

Heptyl(phenyl)(phenylethynyl)phosphine oxide (3ak)



Colorless oil (50 mg, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.89 (dd, *J* = 13.2, 7.2 Hz, 2H), 7.57–7.56 (m, 3H), 7.53–7.50 (m, 2H), 7.47–7.43 (m, 1H), 7.39–7.36 (m, 2H), 2.16–2.10 (m, 2H), 1.71–1.67 (m, 2H), 1.43–1.38 (m, 2H), 1.30–1.23 (m, 6H), 0.86–0.84 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.6 (d, *J* = 114.6 Hz), 132.4, 132.1 (d, *J* = 2.3 Hz), 130.5 (d, *J* = 10.7 Hz), 130.4, 128.7 (d, *J* = 12.8 Hz), 128.5, 120.0 (d, *J* = 3.9 Hz), 103.8 (d, *J* = 27.3 Hz), 83.3 (d, *J* = 156.2 Hz), 34.1 (d, *J* = 83.4 Hz), 31.5, 30.6 (d, *J* = 15.9 Hz), 28.7, 22.5, 21.8 (d, *J* = 4.1 Hz), 14.0. ^{31}P NMR (243 MHz, $CDCl_3$): δ 17.12. HRMS (ESI) calcd for $C_{21}H_{25}OP$ $(M+H)^+$: 325.17158; Found: 325.17163.

Reference:

1. T. Wang, S. Chen, A. Shao, M. Gao, Y. Huang, and A. Lei, *Org. Lett.,* 2015, **17**, 118.

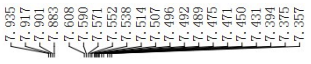
2. J.-Q. Zhang, T. Chen, J.-S. Zhang, and L.-B. Han, *Org. Lett.,* 2017, **19**, 4692.

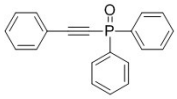
3. H.-M. Guo, Q.-Q. Zhou, X. Jiang, D.-Q. Shi, and W.-J. Xiao, *Adv. Synth. Catal.,* 2017*,* **359**, 4141.

4. L. Peng, F. Xu, Y. Suzuma, A. Orita, and J. Otera, *J. Org. Chem.,* 2013, **78**, 12802.

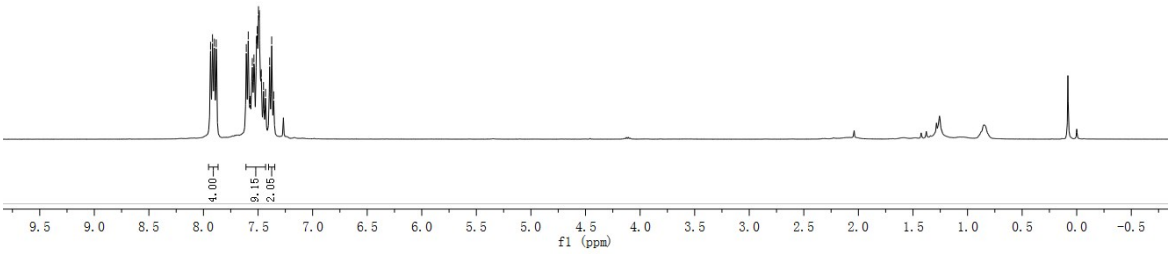
5. J. Yang, T. Chen, Y. Zhou, S. Yin, and L.-B. Han, *Chem. Commun.*, 2015, **51**, 3549.

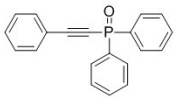
8. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of the products



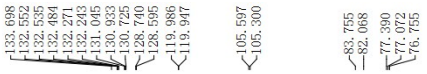


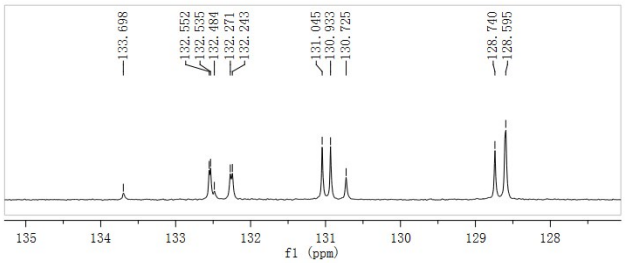
3aa

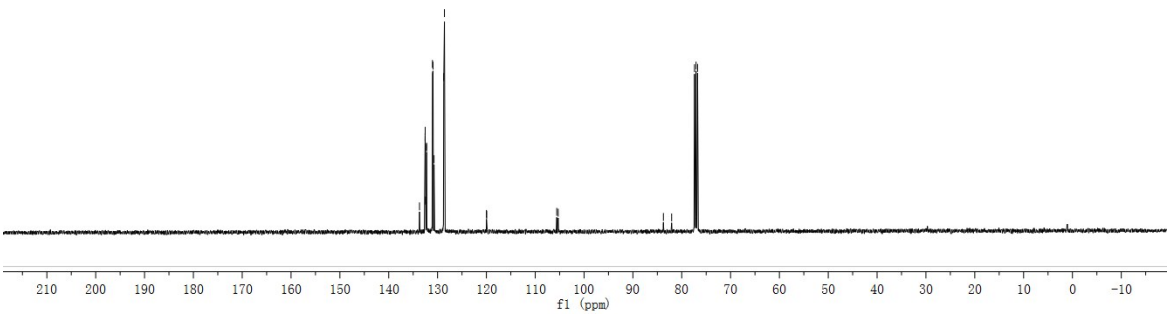


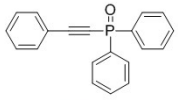


3aa



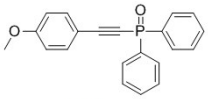






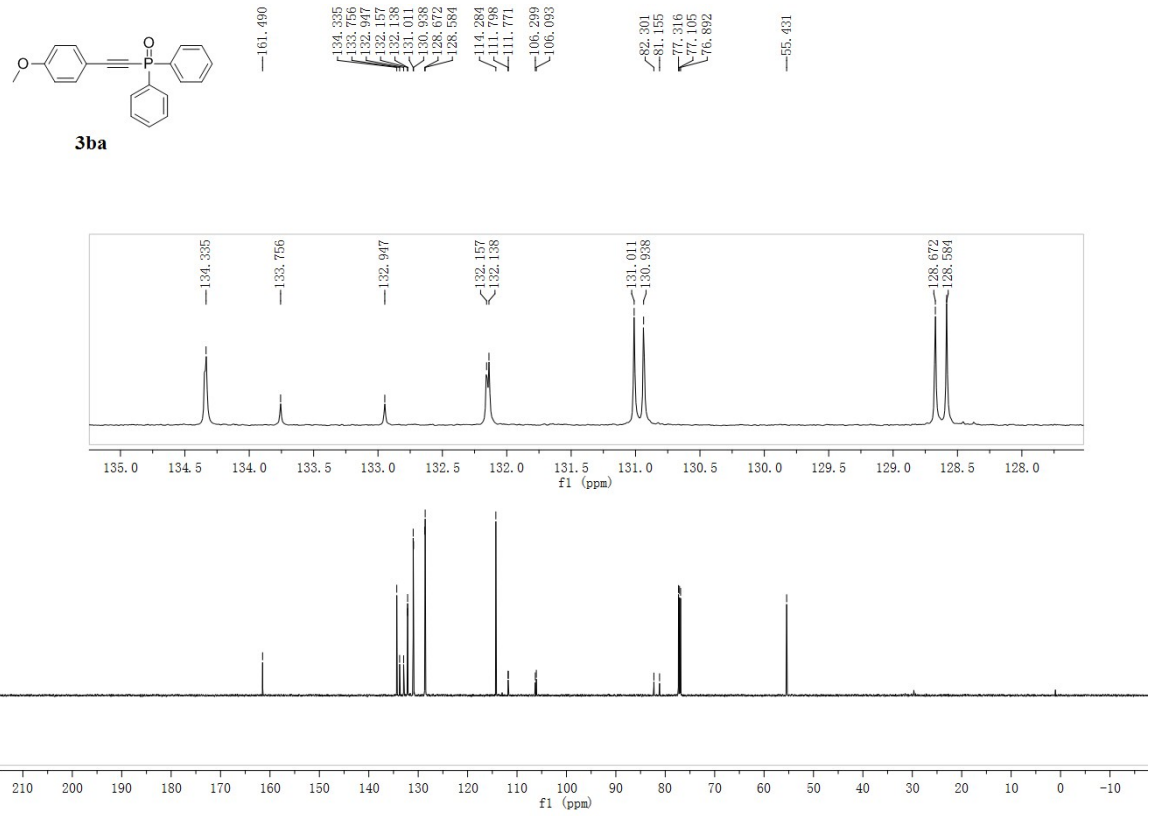
3aa

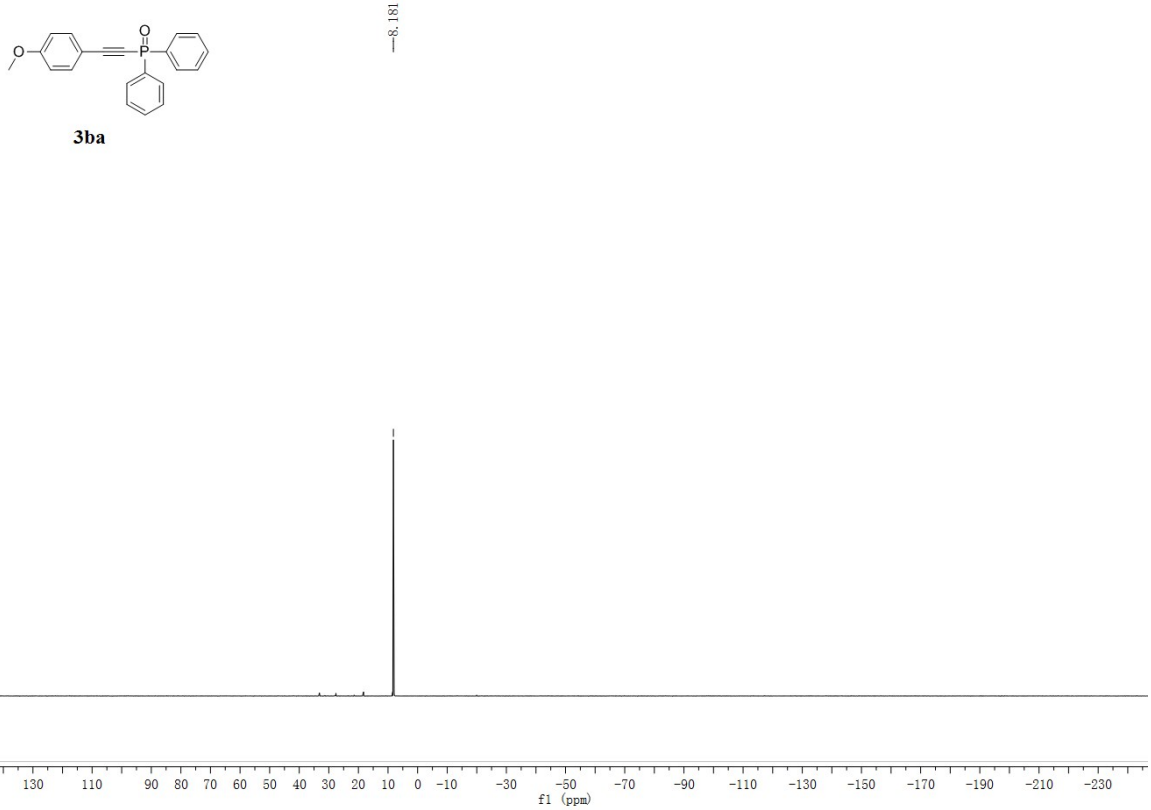
8.313
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

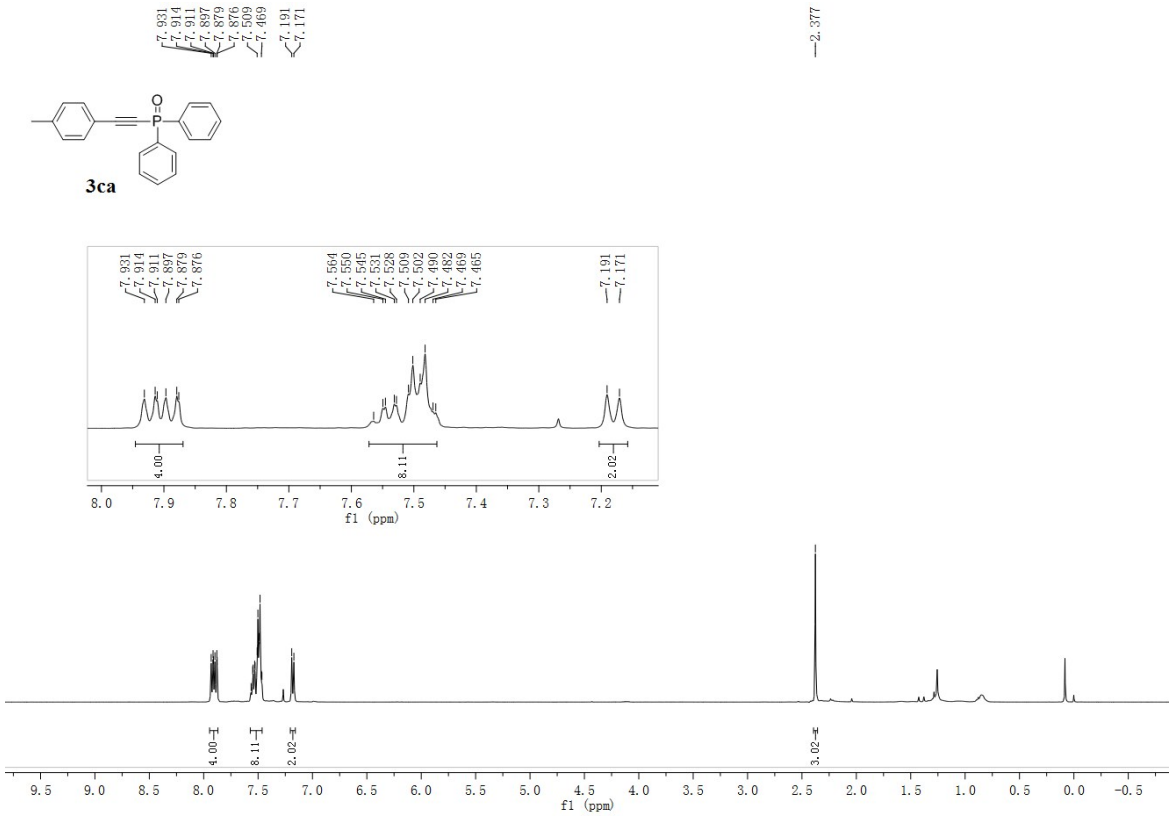


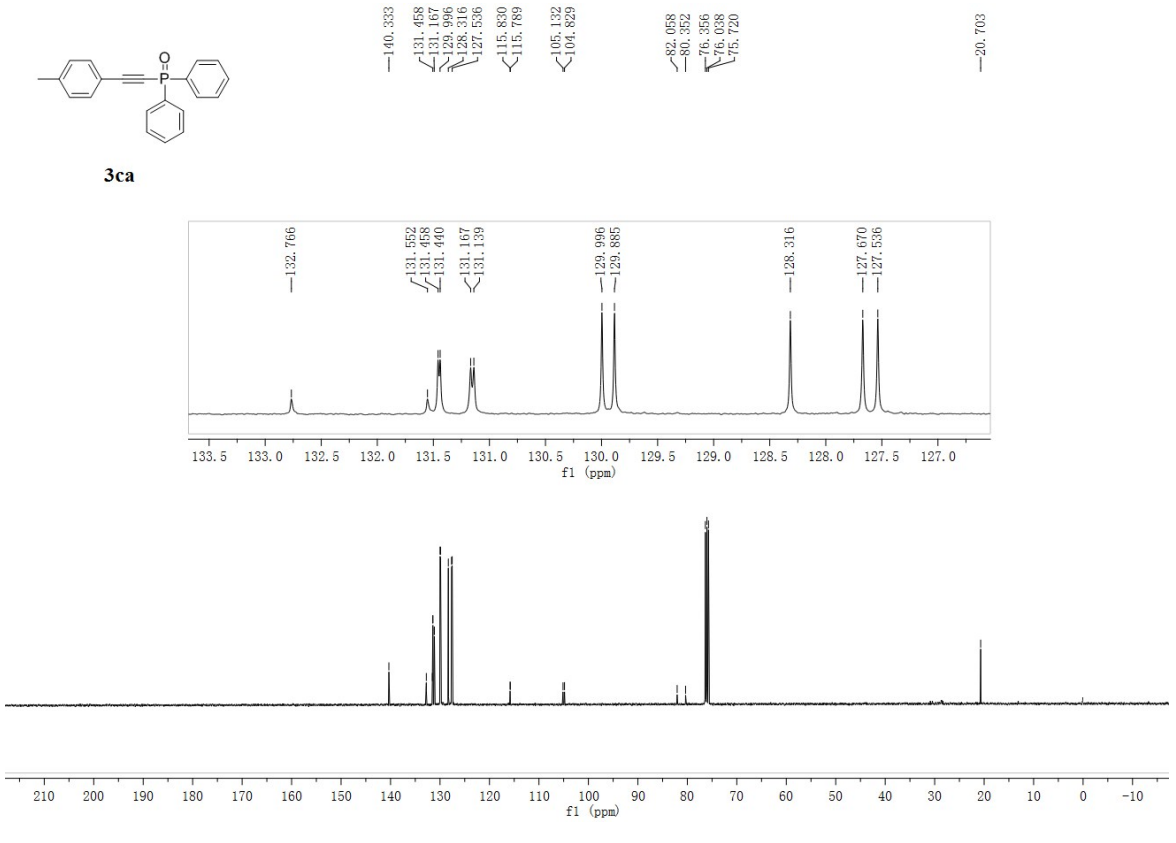
3ba

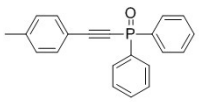
7.920
7.907
7.897
7.884
7.541
7.469
7.272
6.886
6.872
3.817
4.00
8.06
2.07
3.04
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.490
134.335
133.756
132.947
132.157
132.138
131.011
130.938
128.672
128.584
114.284
111.798
111.771
106.299
106.093
82.301
81.155
77.316
77.105
76.892
55.431
3ba
134.335
133.756
132.947
132.157
132.138
131.011
130.938
128.672
128.584
f1 (ppm)
f1 (ppm)


8.181
3ba
f1 (ppm)

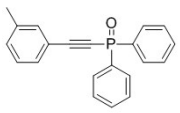

7.931
7.914
7.911
7.897
7.879
7.876
7.509
7.469
7.191
7.171
2.377
3ca
7.564
7.550
7.545
7.531
7.528
7.509
7.502
7.490
7.482
7.469
7.465
4.00
8.11
2.02
f1 (ppm)
3.02


140.333
131.458
131.167
129.996
128.316
127.536
115.830
115.789
105.132
104.829
82.058
80.352
76.356
76.038
75.720
20.703
3ca
132.766
131.552
131.458
131.440
131.167
131.139
129.996
129.885
128.316
127.670
127.536
f1 (ppm)



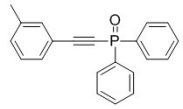
3ca

8.329
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



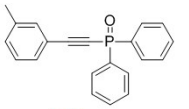
3da

7.932
7.915
7.911
7.898
7.880
7.877
7.532
7.486
7.398
7.267
7.258
7.255
2.347
7.569
7.554
7.550
7.536
7.532
7.513
7.505
7.494
7.490
7.486
7.477
7.473
7.469
7.417
7.398
4.00
6.03
2.06
2.08
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
4.00
6.03
2.06
2.08
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



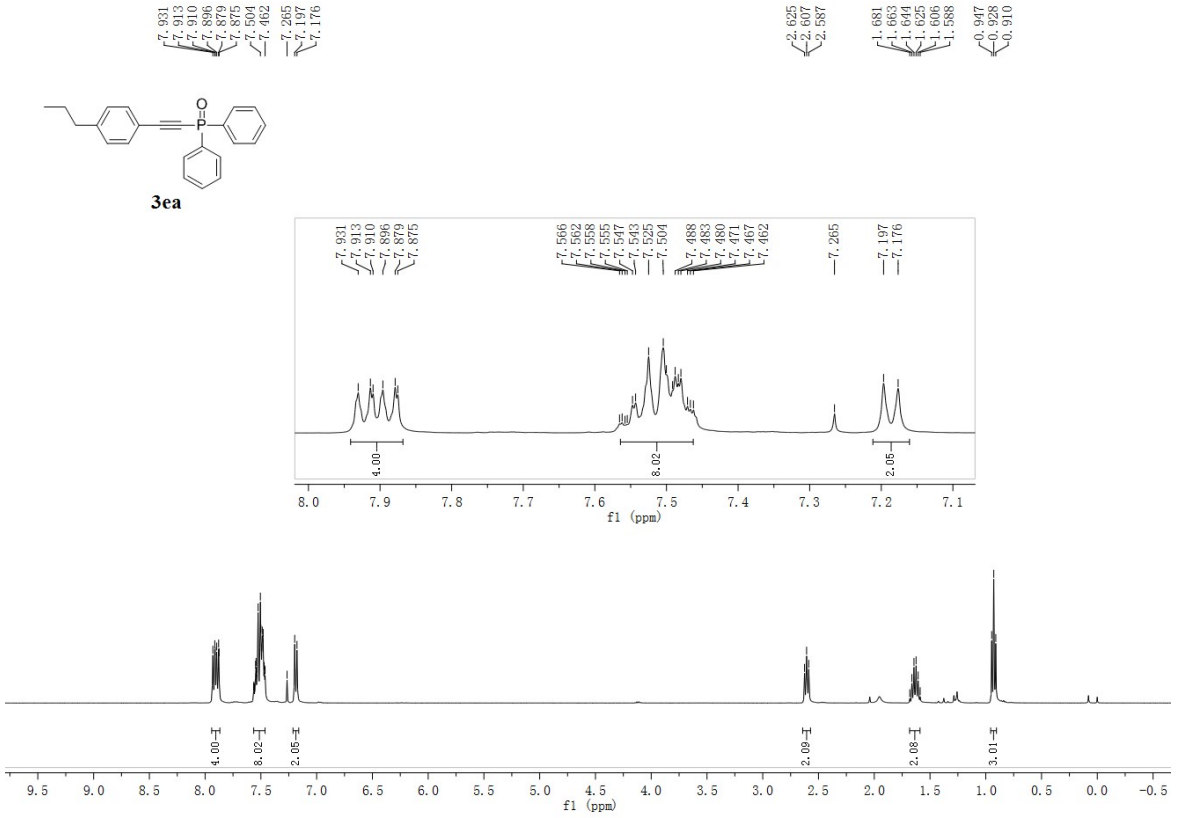
3da

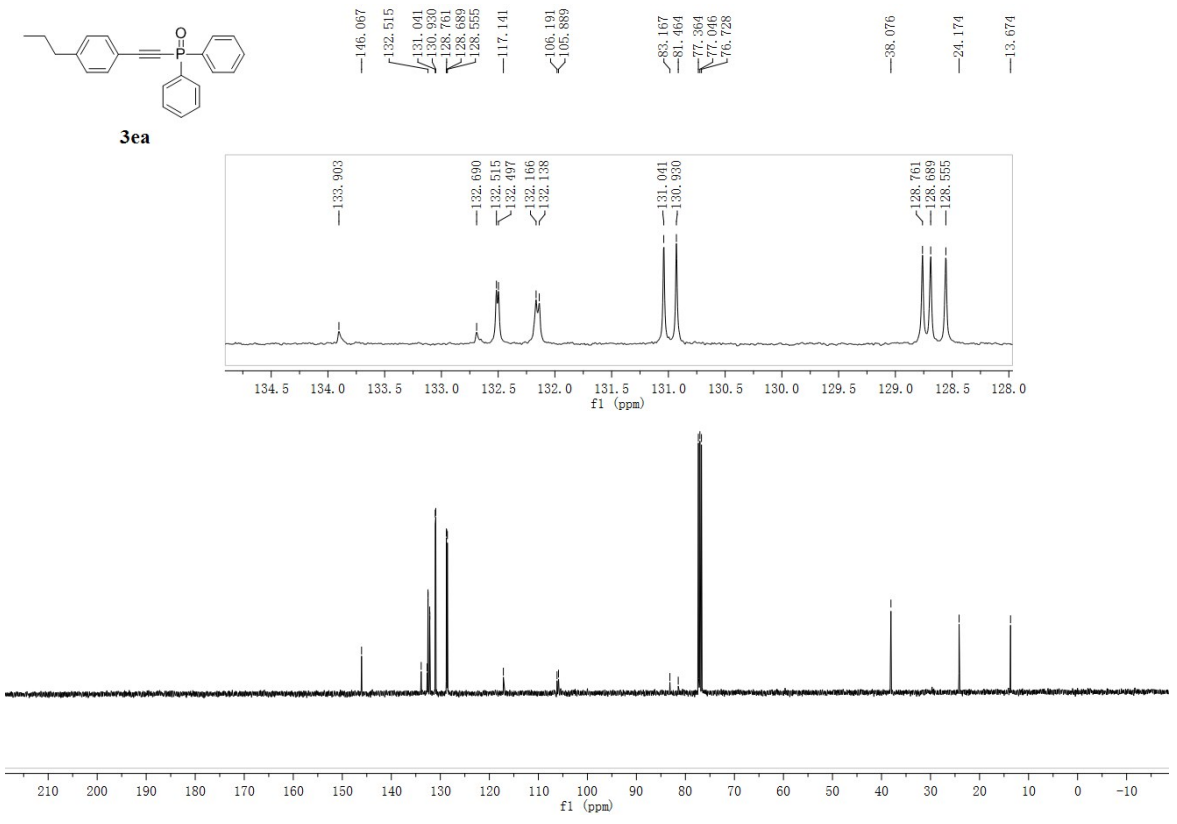
138.441
132.226
131.043
129.679
128.494
119.786
119.744
105.953
105.654
83.353
81.656
77.382
77.065
76.747
21.174
138.441
133.786
132.985
132.966
132.573
132.226
132.198
131.652
131.043
130.932
129.698
129.679
128.721
128.588
128.494
f1 (ppm)
f1 (ppm)

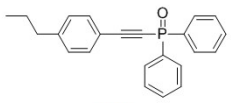


3da

8.257
f1 (ppm)

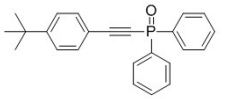

7.931
7.913
7.910
7.896
7.879
7.875
7.504
7.462
7.265
7.197
7.176
2.625
2.607
2.587
1.681
1.663
1.644
1.625
1.606
1.588
0.947
0.928
0.910
O
P
3ea
4.00
8.02
2.05
2.09
2.08
3.01
f1 (ppm)


146.067
132.515
131.041
130.930
128.761
128.689
128.555
117.141
106.191
105.869
83.167
81.464
77.364
77.046
76.728
38.076
24.174
13.674
O
P
3ea
133.903
132.690
132.515
132.497
132.166
132.138
131.041
130.930
128.761
128.689
128.555
f1 (ppm)



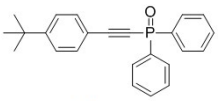
3ea

8.251
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

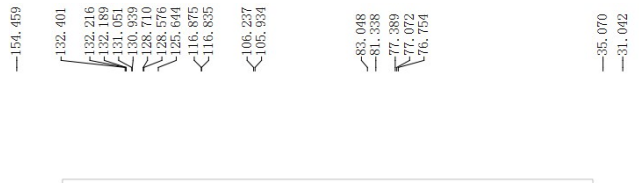


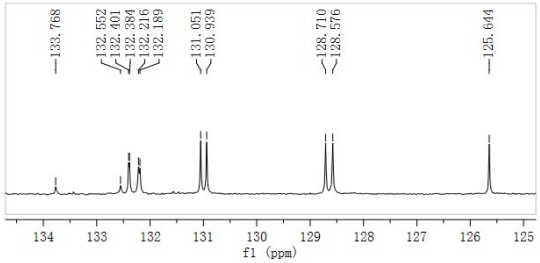
3fa

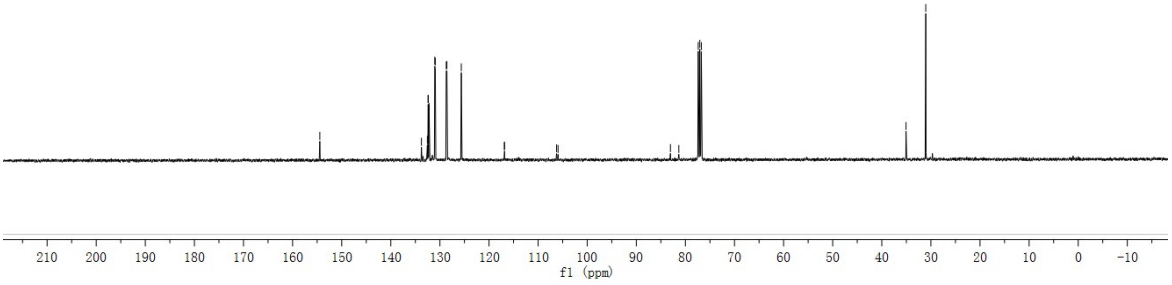
7.932
7.914
7.897
7.879
7.553
7.532
7.503
7.496
7.485
7.410
7.389
7.265
1.312
4.00
8.06
2.04
9.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

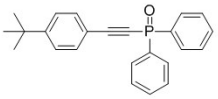


3fa


154.459
132.401
132.216
132.189
131.051
130.939
128.710
128.576
125.644
116.875
116.835
106.237
105.934
83.048
81.338
77.389
77.072
76.754
35.070
31.042

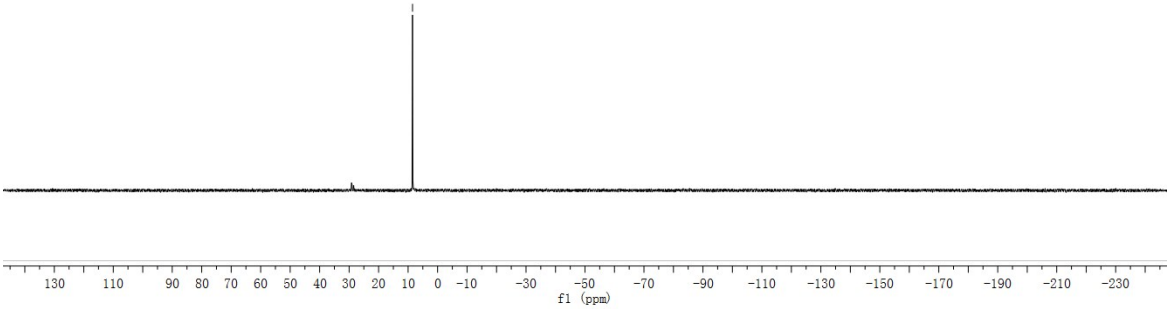

133.768
132.552
132.401
132.384
132.216
132.189
131.051
130.939
128.710
128.576
125.644
134
133
132
131
130
129
128
127
126
125
f1 (ppm)

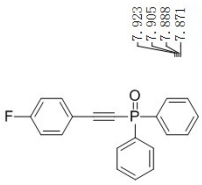

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



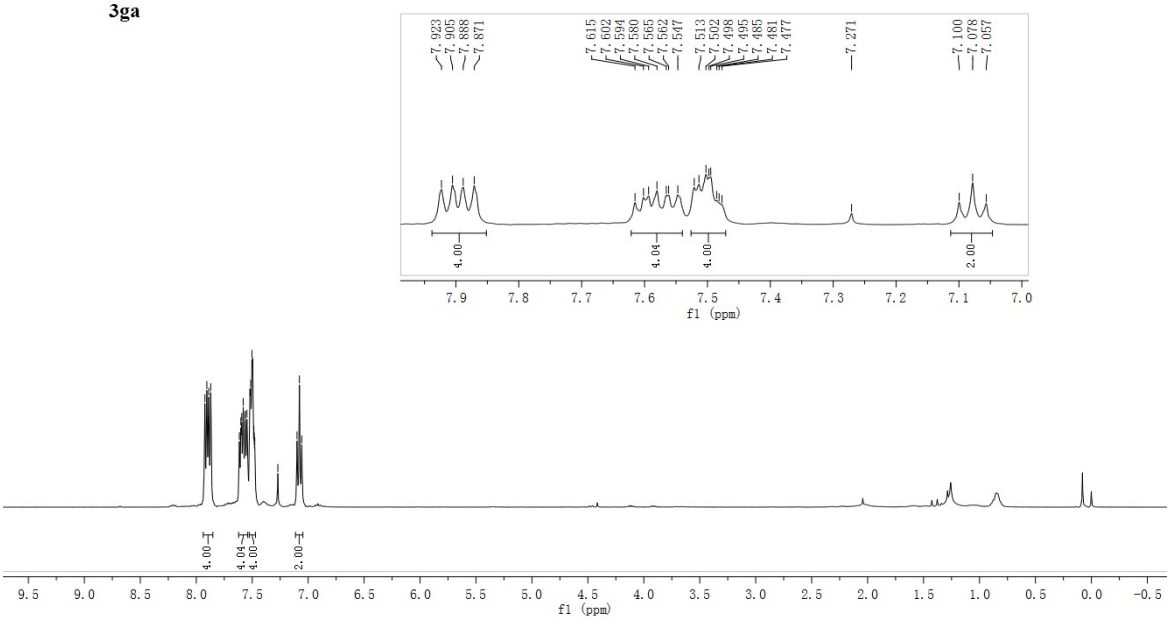
3fa

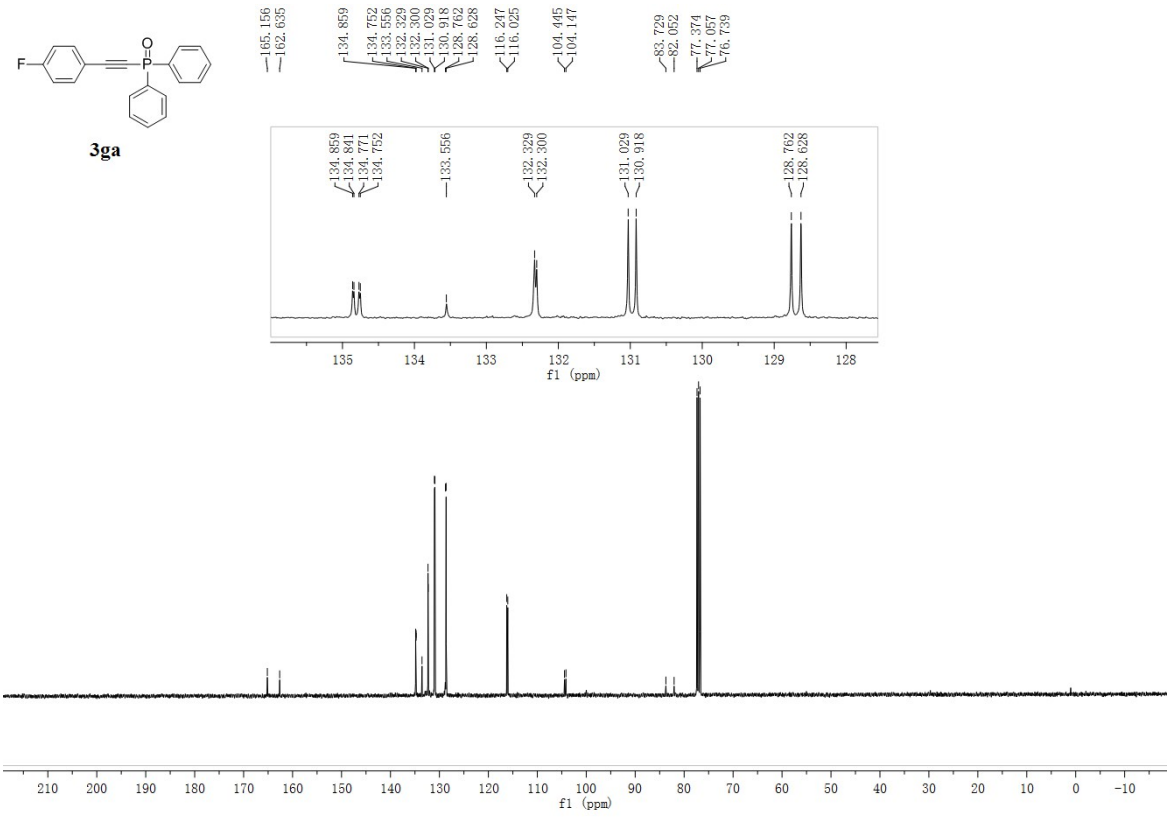

8.498


130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

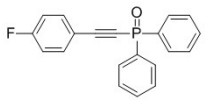


3ga



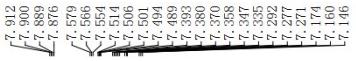


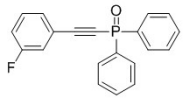
3ga



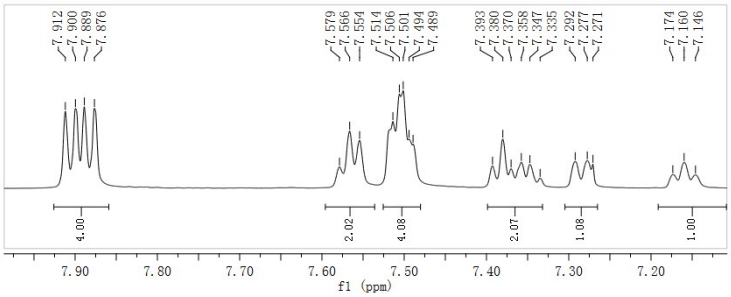
3ga

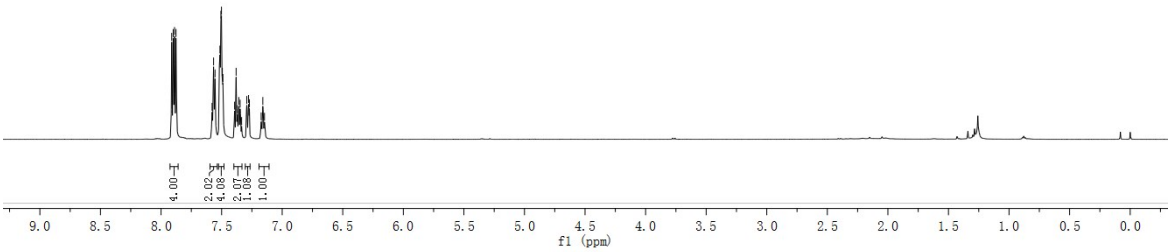
8.308
f1 (ppm)

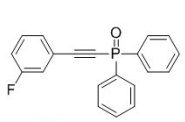

7.912
7.900
7.889
7.876
7.579
7.566
7.554
7.514
7.506
7.501
7.494
7.489
7.393
7.380
7.370
7.358
7.347
7.335
7.292
7.277
7.271
7.174
7.160
7.146



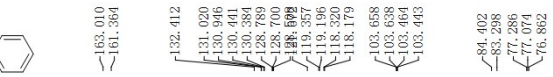
3ha

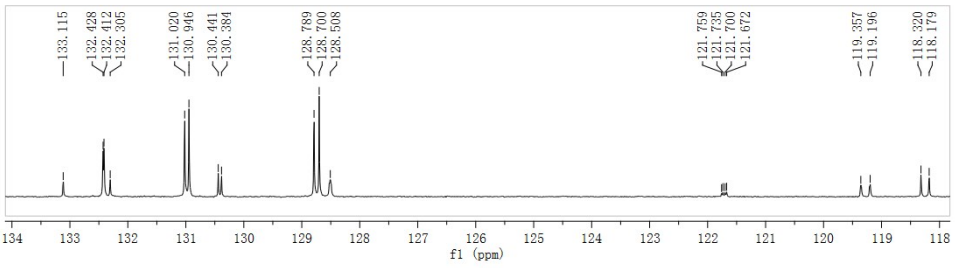

7.912
7.900
7.889
7.876
7.579
7.566
7.554
7.514
7.506
7.501
7.494
7.489
7.393
7.380
7.370
7.358
7.347
7.335
7.292
7.277
7.271
7.174
7.160
7.146
4.00
2.02
4.08
2.07
1.08
1.00
f1 (ppm)

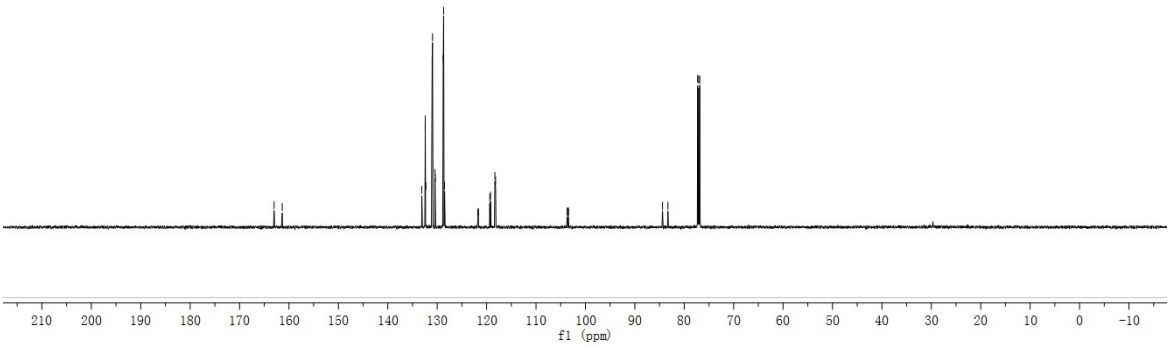

4.00
2.02
4.08
2.07
1.08
1.00
f1 (ppm)

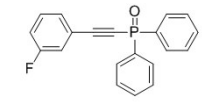


3ha


163.010
161.364
132.412
131.020
130.946
130.441
130.384
128.789
128.700
119.357
119.196
118.320
118.179
103.658
103.638
103.464
103.443
84.402
83.298
77.286
77.074
76.862

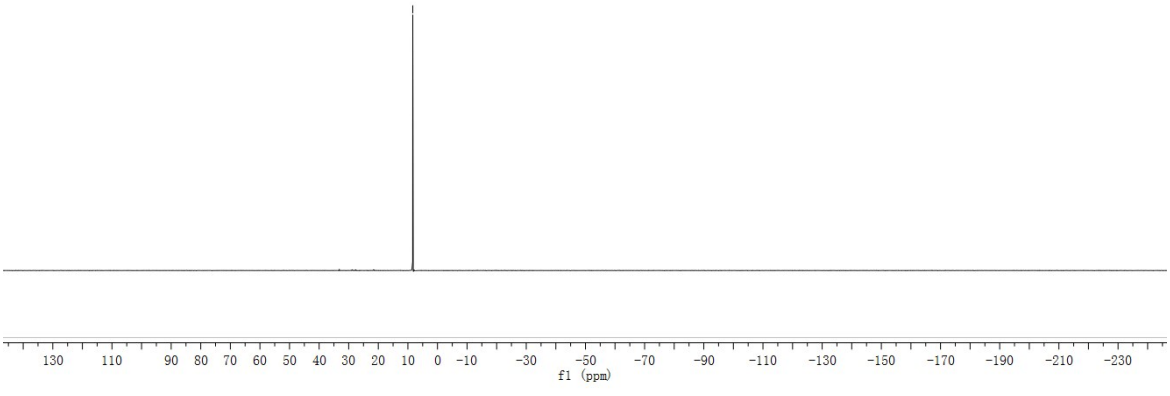

133.115
132.428
132.412
132.305
131.020
130.946
130.441
130.384
128.789
128.700
128.508
121.759
121.735
121.700
121.672
119.357
119.196
118.320
118.179
f1 (ppm)

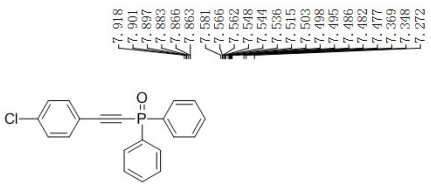

f1 (ppm)



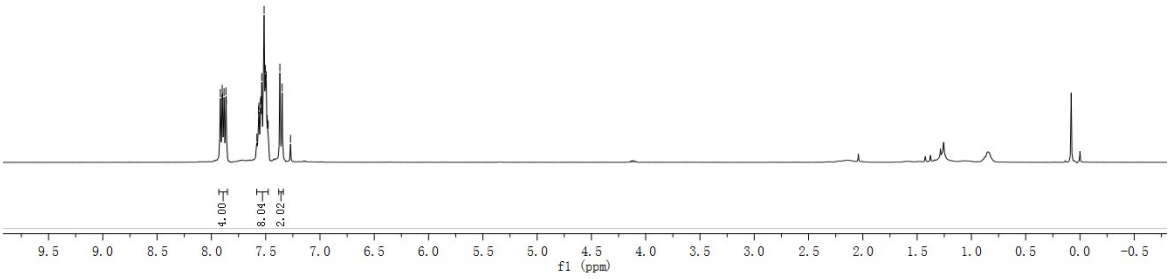
3ha

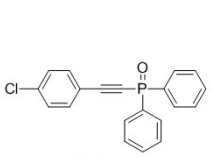

8.348


f1 (ppm)


7.918
7.901
7.897
7.883
7.866
7.863
7.581
7.566
7.562
7.548
7.544
7.536
7.515
7.503
7.498
7.495
7.486
7.482
7.477
7.369
7.348
7.272
O
Cl
P

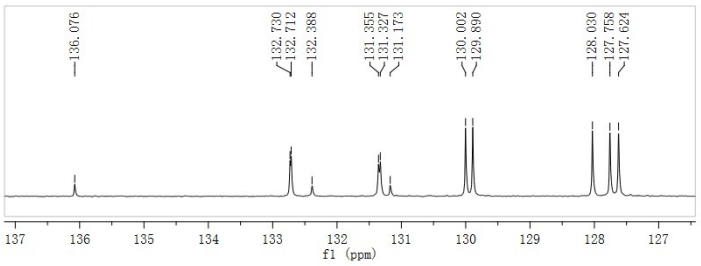
3ia

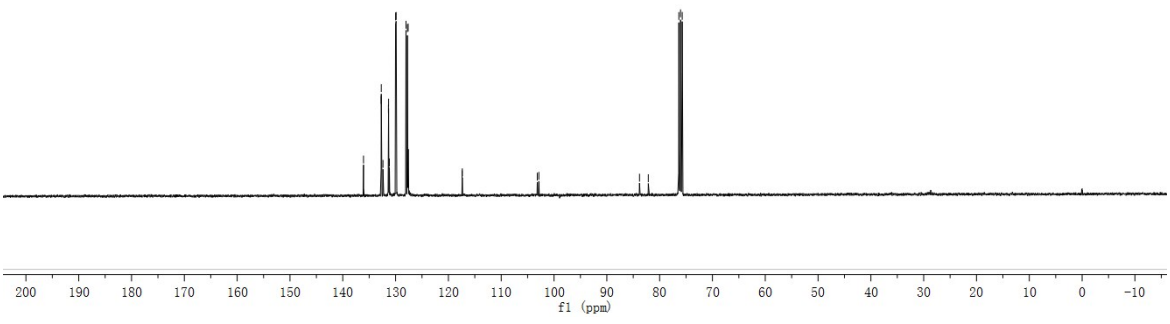

4.00
8.04
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

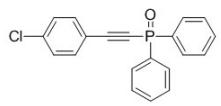

O
Cl
P

3ia


136.076
132.712
130.002
128.030
127.624
117.406
117.366
103.165
102.871
83.810
82.147
76.359
76.041
75.723


136.076
132.730
132.712
132.388
131.355
131.327
131.173
130.002
129.890
128.030
127.758
127.624
137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)

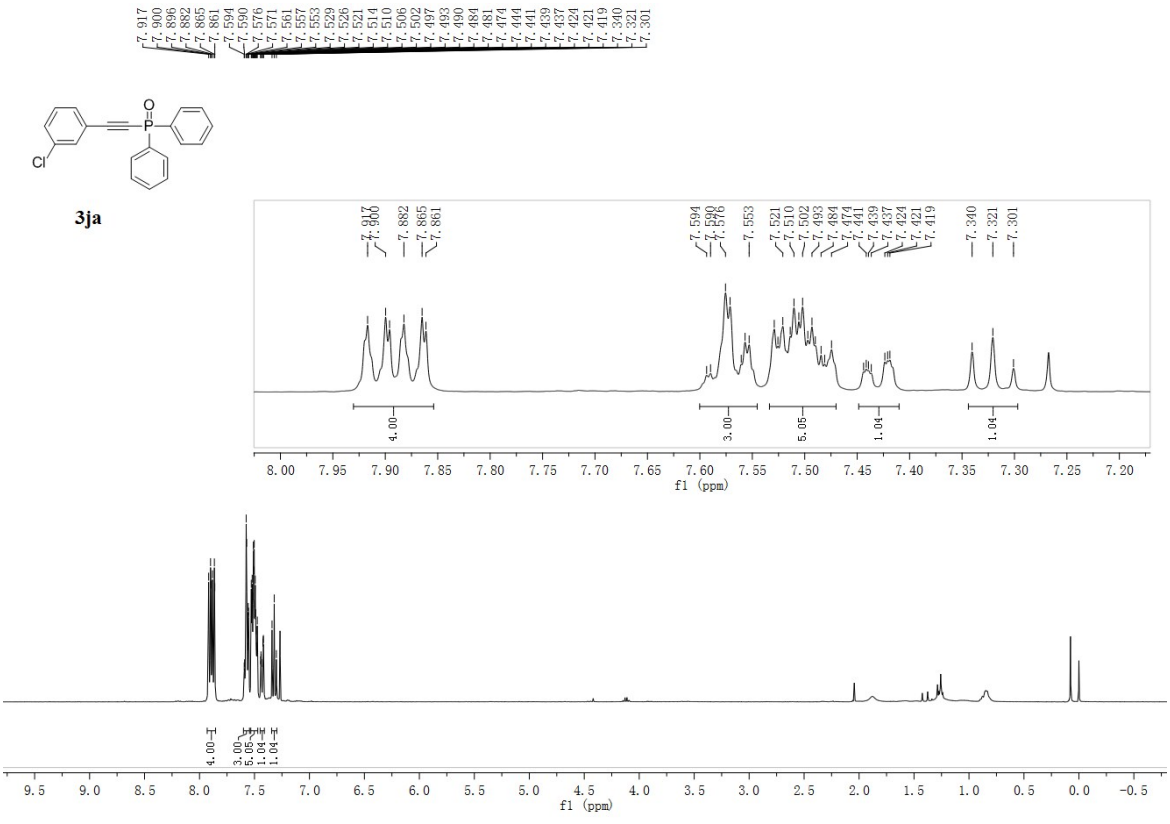

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3ia

8.366
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

3ja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7.896
7.882
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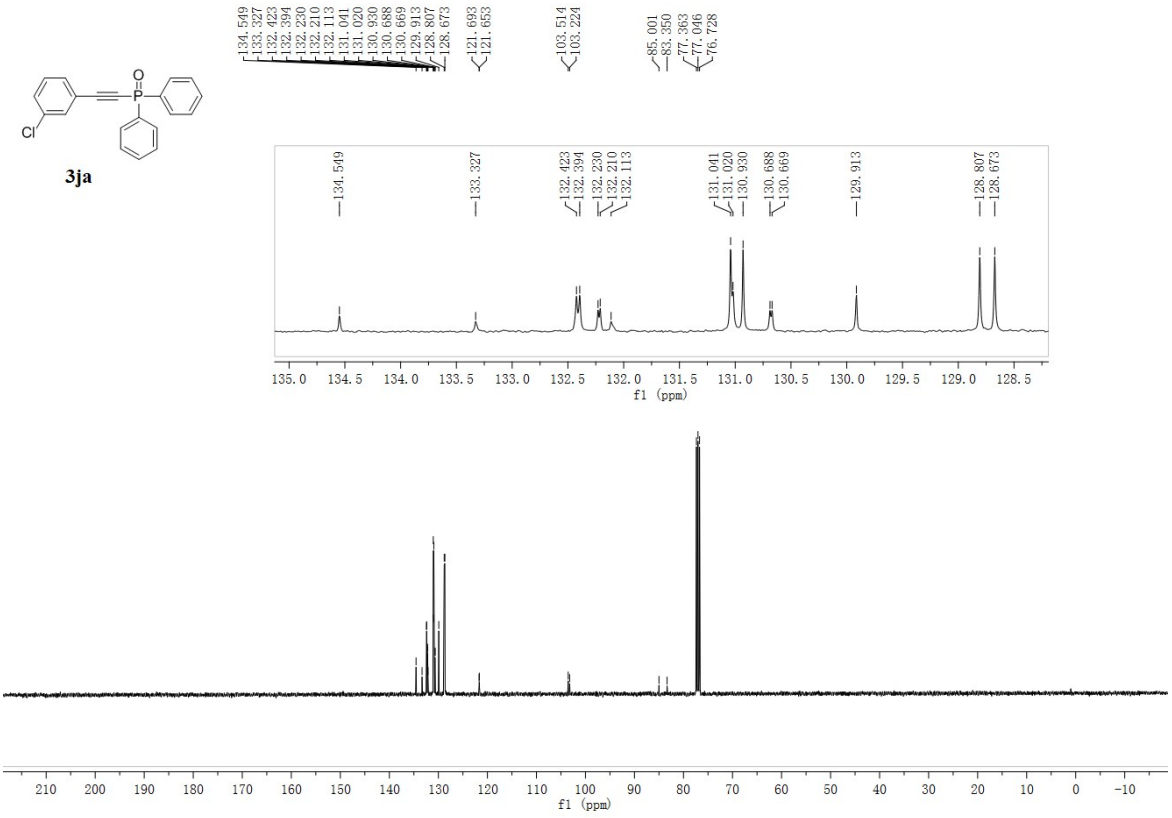
7.594
7.590
7.576
7.571
7.561
7.557
7.553
7.529
7.526
7.521
7.514
7.510
7.506
7.502
7.497
7.493
7.490
7.484
7.481
7.474
7.444
7.441
7.439
7.437
7.424
7.421
7.419
7.340
7.321
7.301
4.00
3.00
5.05
1.04
1.04
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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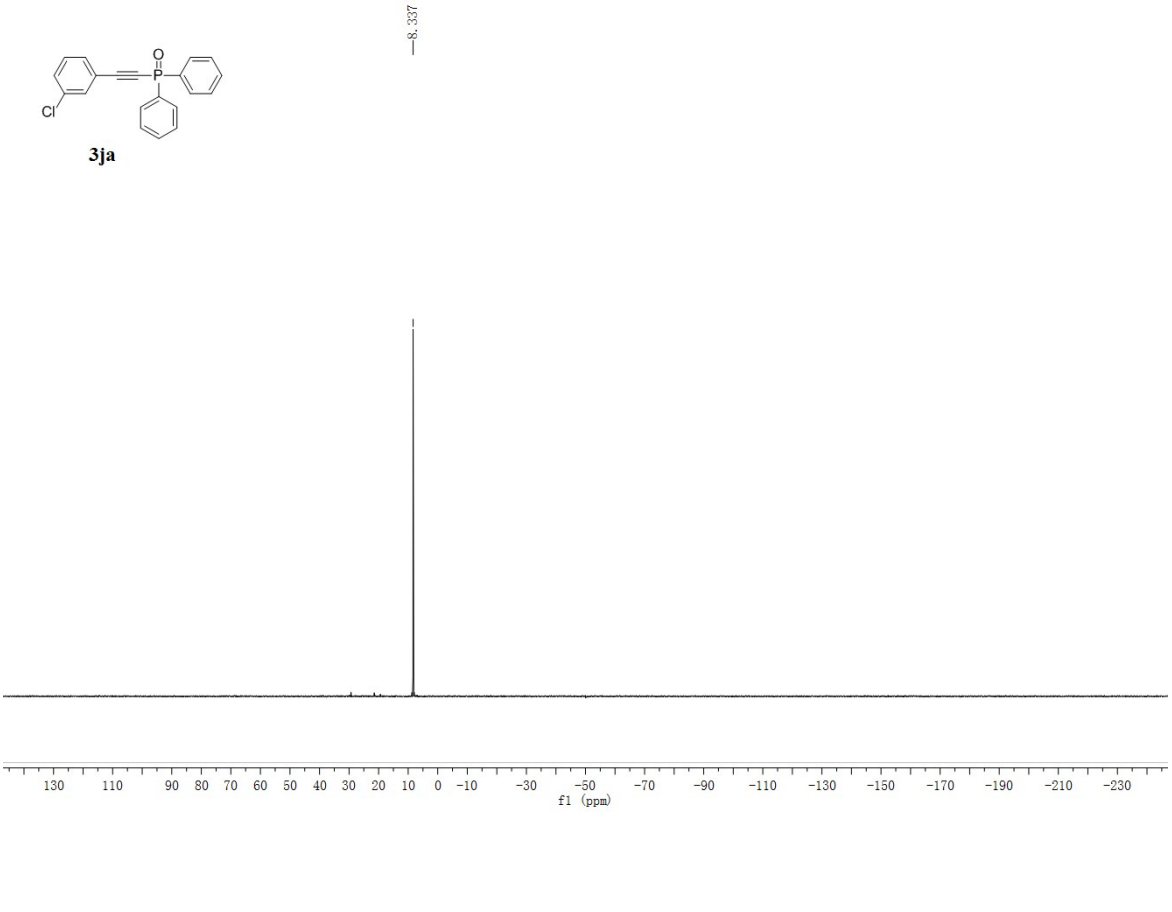
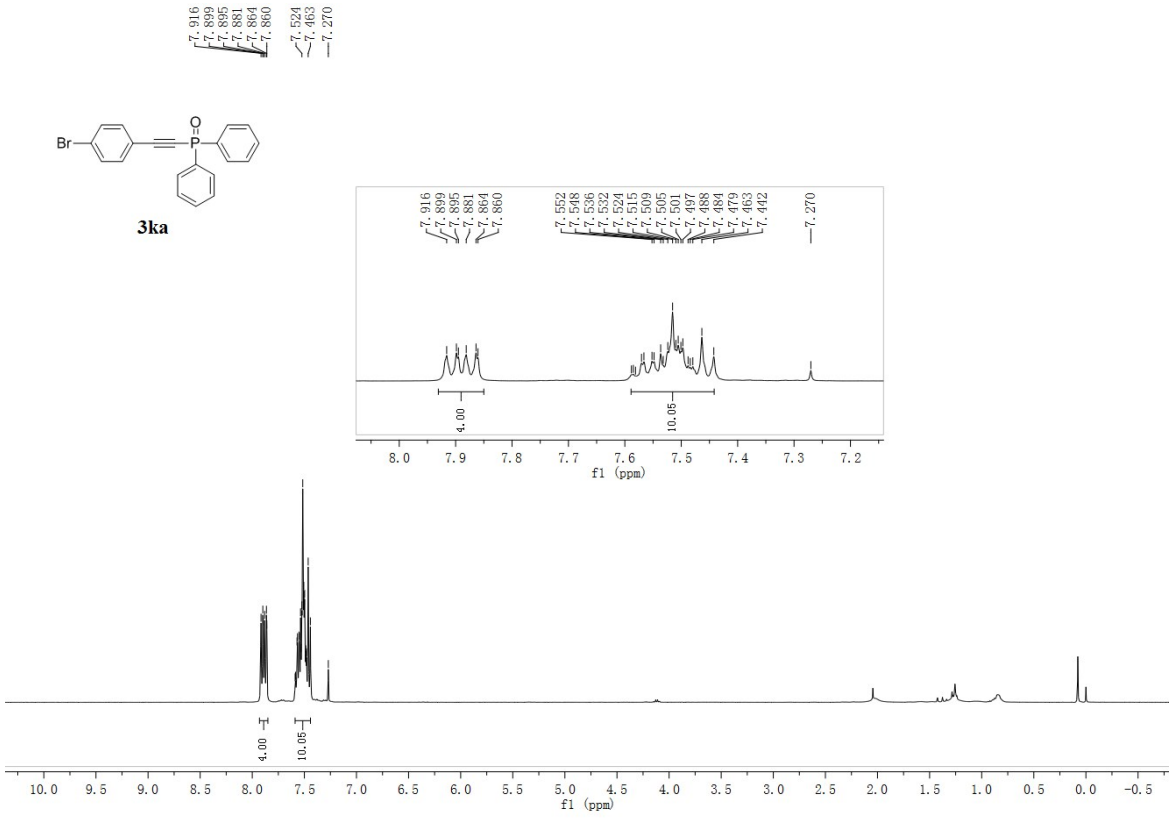
133.327
132.423
132.394
132.230
132.210
132.113
131.041
131.020
130.930
130.688
130.669
129.913
128.807
128.673
121.693
121.653
103.514
103.224
85.001
83.350
77.363
77.046
76.728
Cl
O
P
3ja
f1 (ppm)


8.337
Cl
O
P
3ja
f1 (ppm)


7.916
7.899
7.895
7.881
7.864
7.860
7.524
7.463
7.270
Br
O
P
3ka
7.552
7.548
7.536
7.532
7.524
7.515
7.509
7.505
7.501
7.497
7.488
7.484
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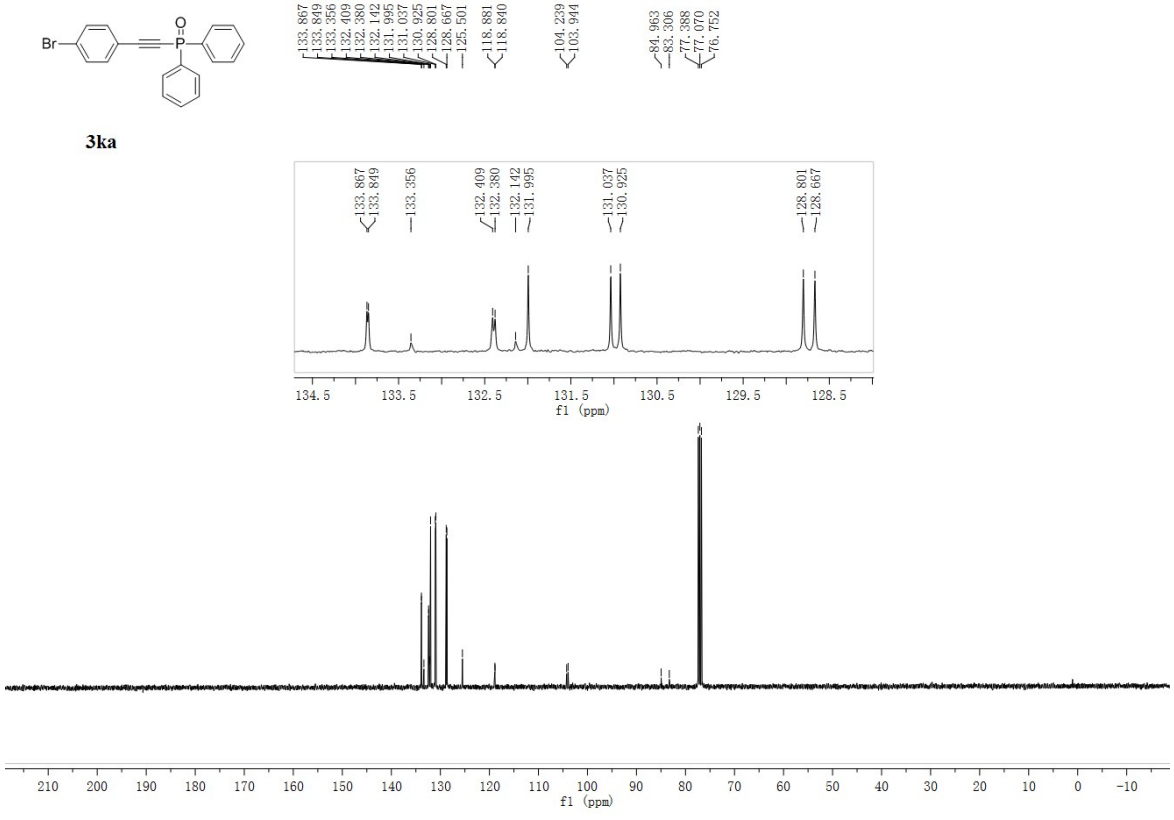
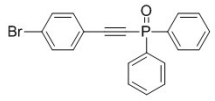
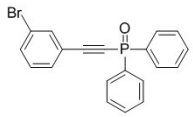
7.463
7.442
4.00
10.05
f1 (ppm)


133.867
133.849
133.356
132.409
132.380
132.142
131.995
131.037
130.925
128.801
128.667
125.501
118.881
118.840
104.239
103.944
84.963
83.306
77.388
77.070
76.752
Br
O
P
3ka
f1 (ppm)

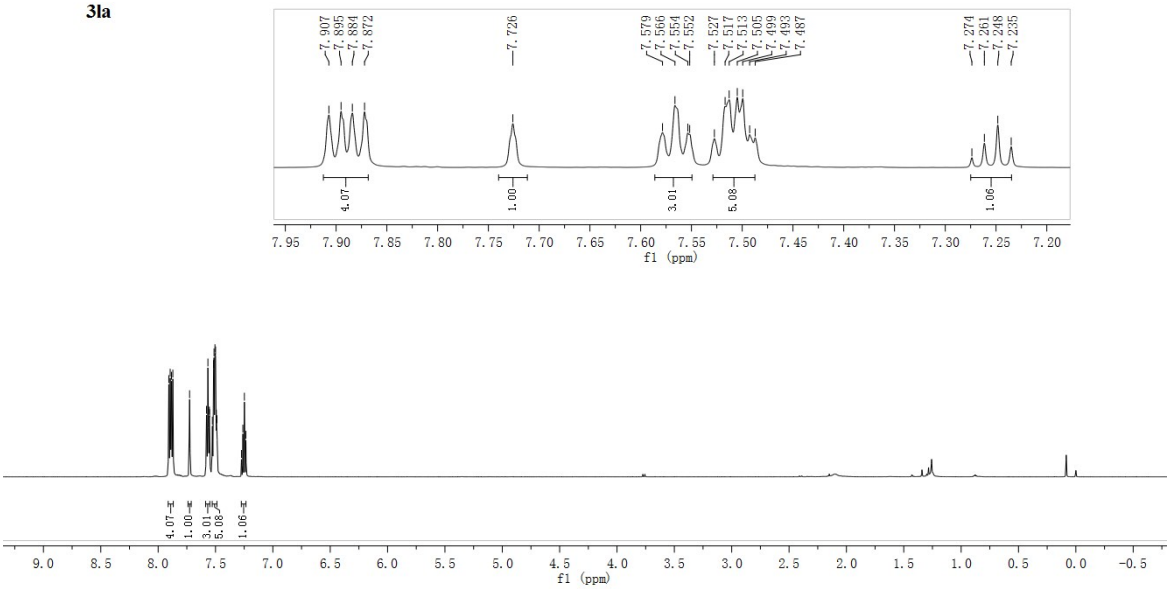


3ka

8.429
f1 (ppm)



3la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7.895
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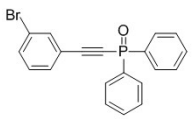
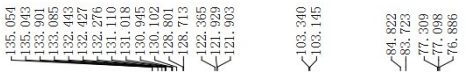
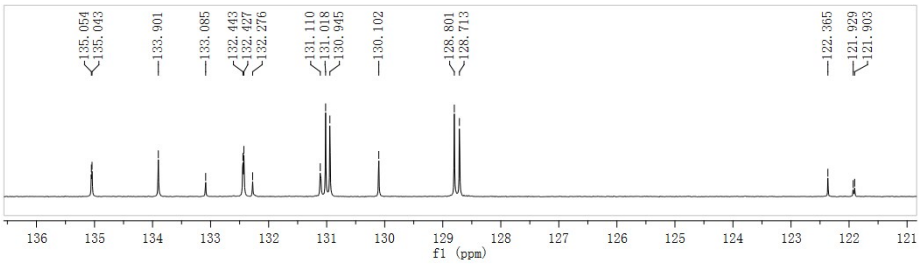
7.579
7.566
7.554
7.552
7.527
7.517
7.513
7.505
7.499
7.493
7.487
7.274
7.261
7.248
7.235
4.07
1.00
3.01
5.08
1.06
f1 (ppm)


Br
O
P

3la


135.054
135.043
133.901
133.085
132.443
132.427
132.276
131.110
131.018
130.945
130.102
128.801
128.713
122.365
121.929
121.903
103.340
103.145
84.822
83.723
77.309
77.098
76.886


135.054
135.043
133.901
133.085
132.443
132.427
132.276
131.110
131.018
130.945
130.102
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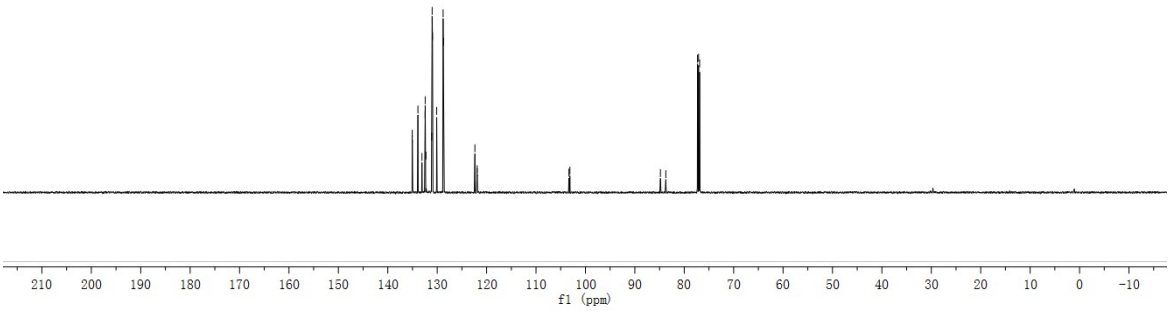
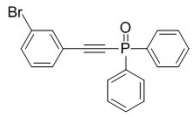
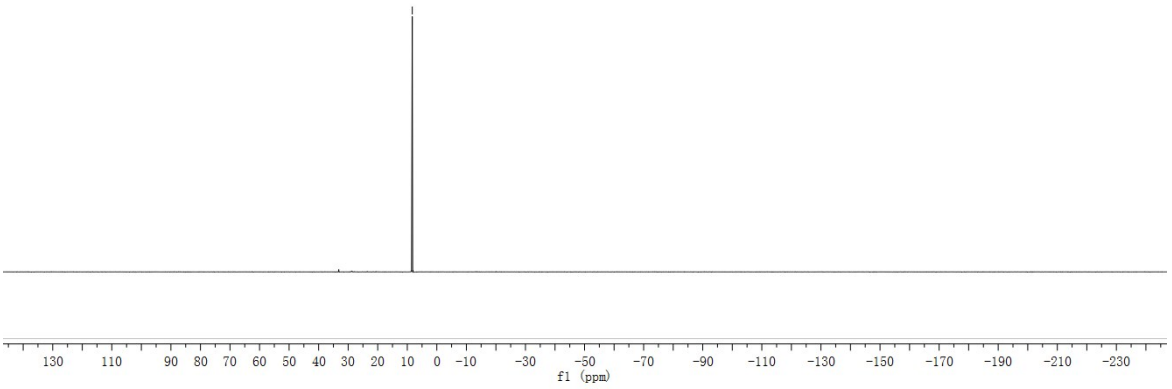
128.713
122.365
121.929
121.903
f1 (ppm)

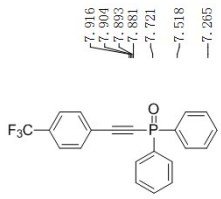

f1 (ppm)


8.311

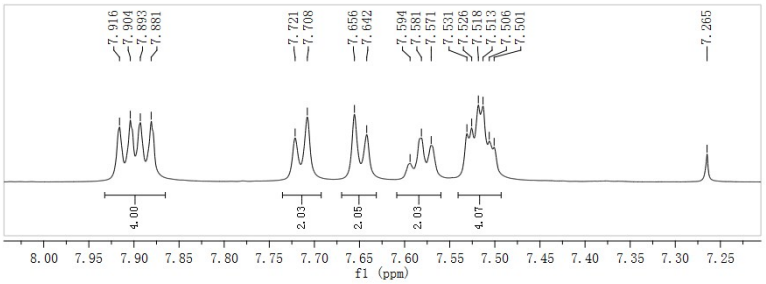

Br
O
P

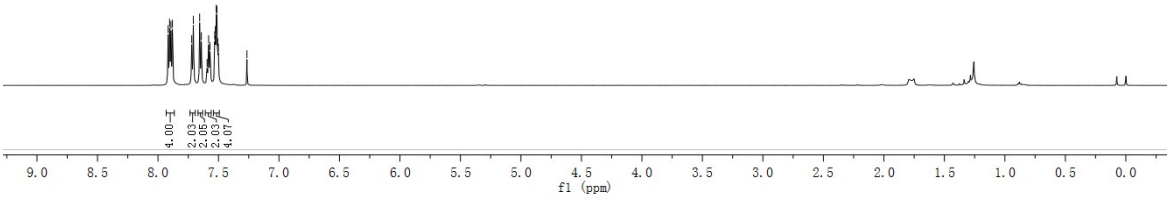
3la

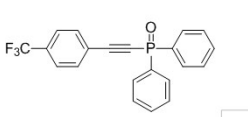

f1 (ppm)



3ma







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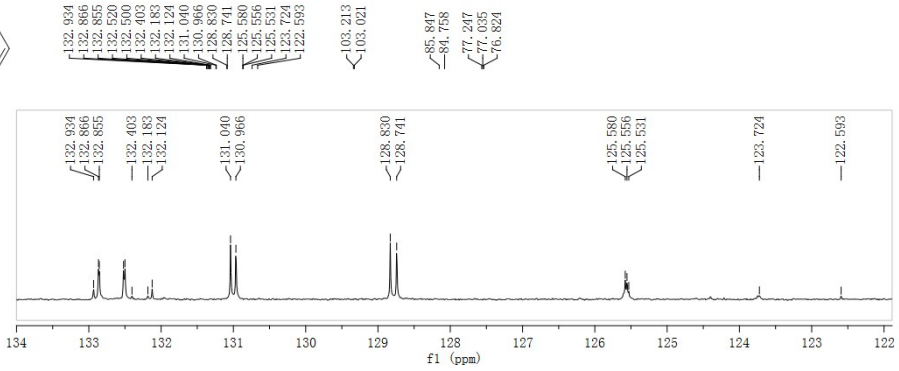
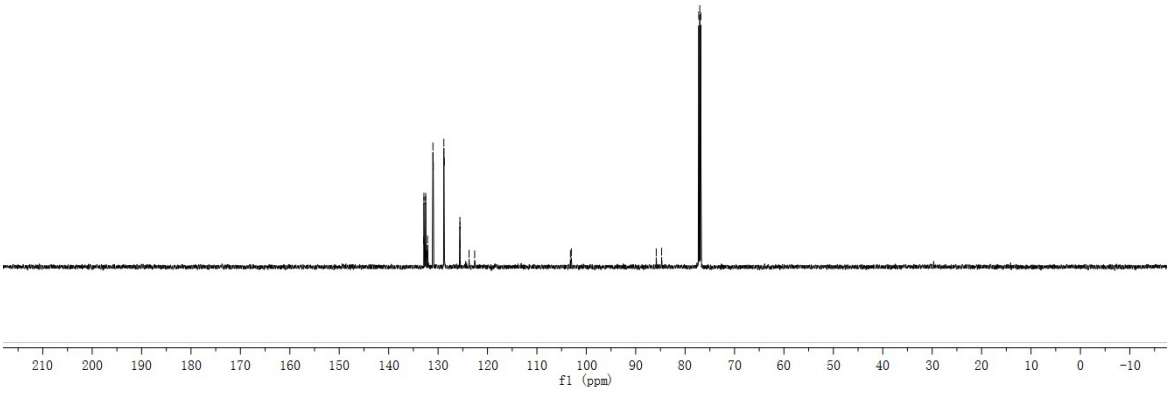
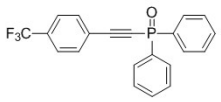
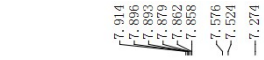


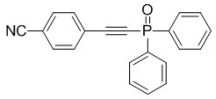




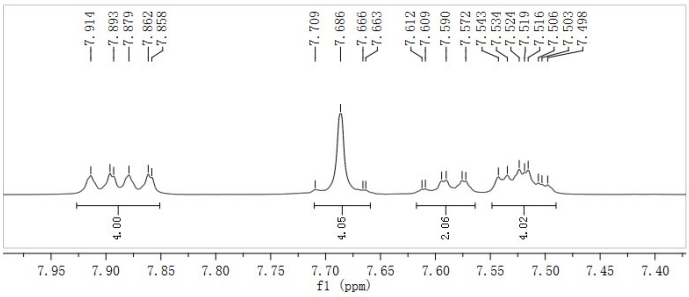
3ma

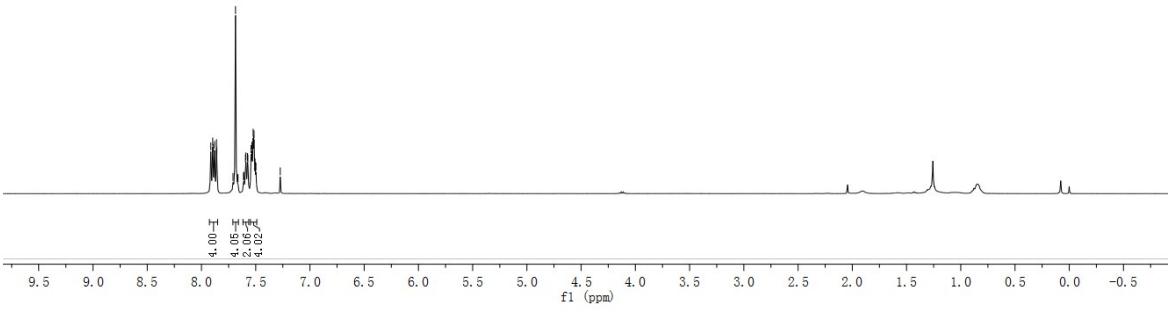
8.409
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

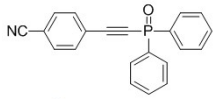

7.914
7.896
7.893
7.879
7.862
7.858
7.576
7.524
7.274



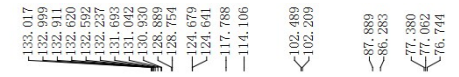
3na


7.914
7.893
7.879
7.862
7.858
7.709
7.686
7.666
7.663
7.612
7.609
7.590
7.572
7.543
7.534
7.524
7.519
7.516
7.506
7.503
7.498
4.00
4.06
2.06
4.02
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
f1 (ppm)


4.00
4.06
2.06
4.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


NC
O
P

3na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132.911
132.620
132.592
132.237
131.693
131.042
130.930
128.889
128.754
124.679
124.641
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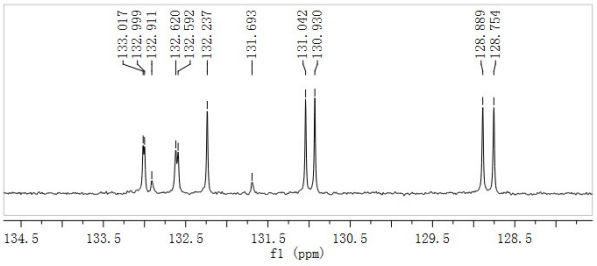
114.106
102.489
102.209
87.889
86.283
77.380
77.062
76.744


133.017
132.999
132.911
132.620
132.592
132.237
131.693
131.042
130.930
128.889
128.754
134.5
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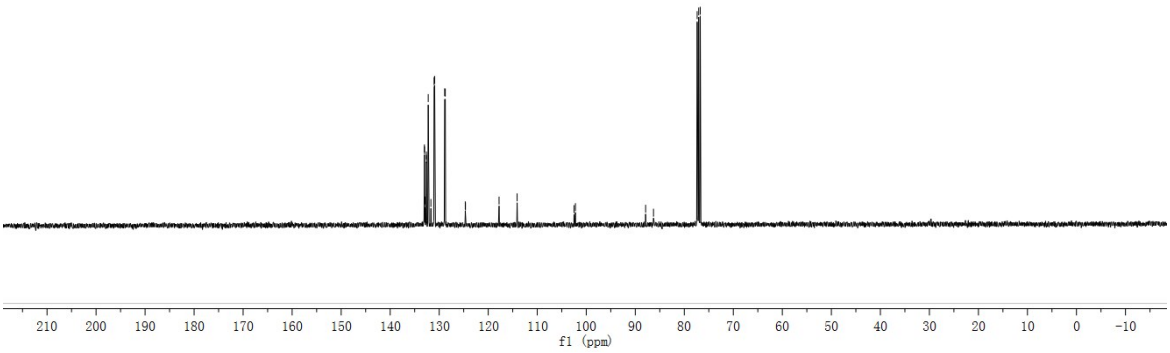
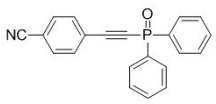
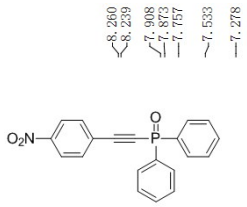
131.5
130.5
129.5
128.5
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

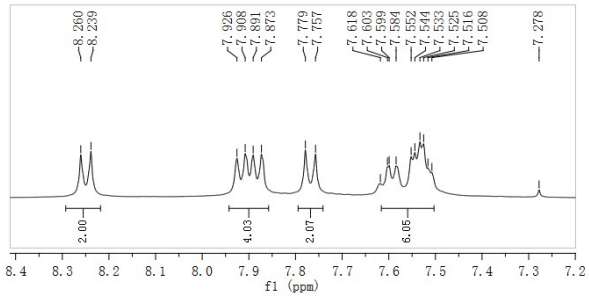

NC
O
P

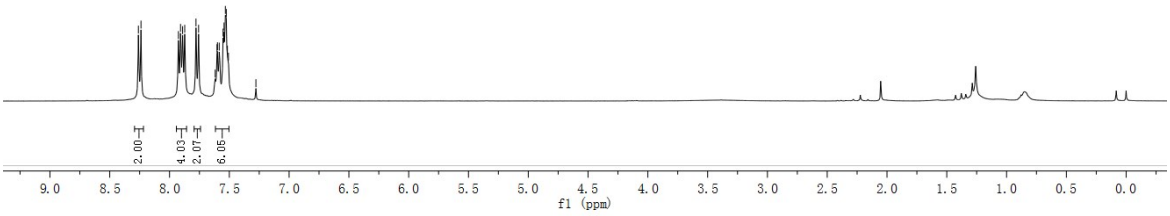
3na

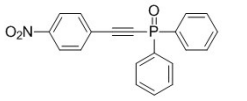
8.461
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)



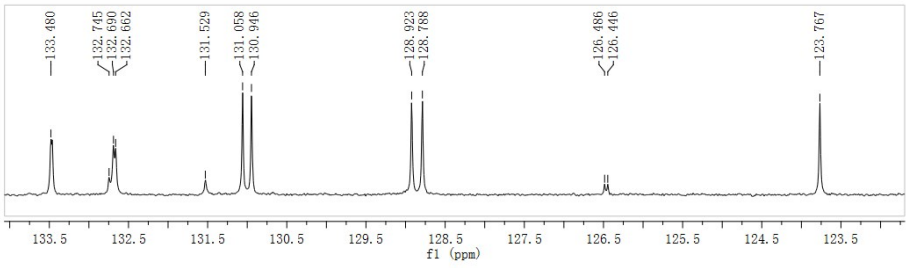
3oa

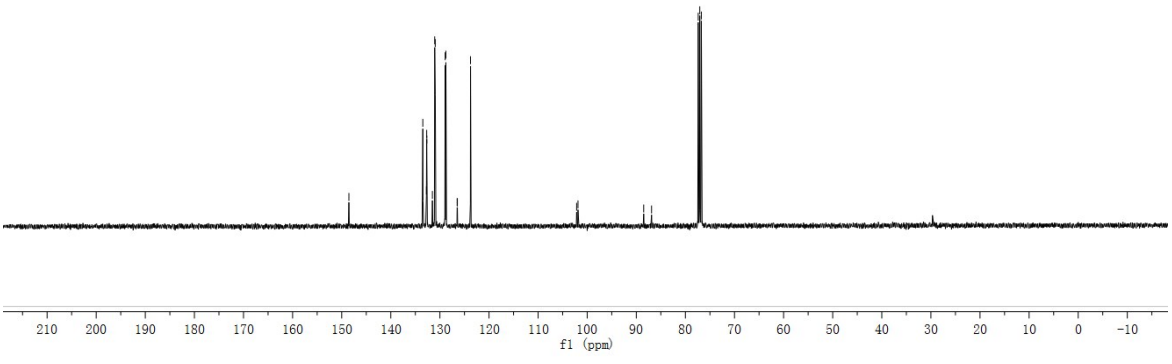


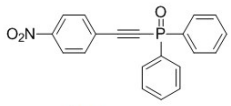




3oa







3oa

8.643
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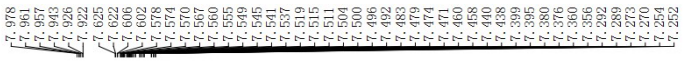
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)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7.957
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7.922
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7.622
7.606
7.602
7.578
7.574
7.570
7.567
7.560
7.555
7.549
7.545
7.541
7.537
7.519
7.515
7.511
7.504
7.500
7.496
7.492
7.483
7.479
7.474
7.471
7.460
7.458
7.440
7.438
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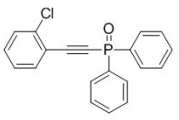
7.252



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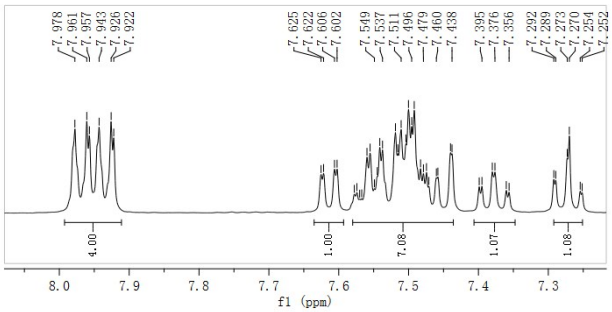
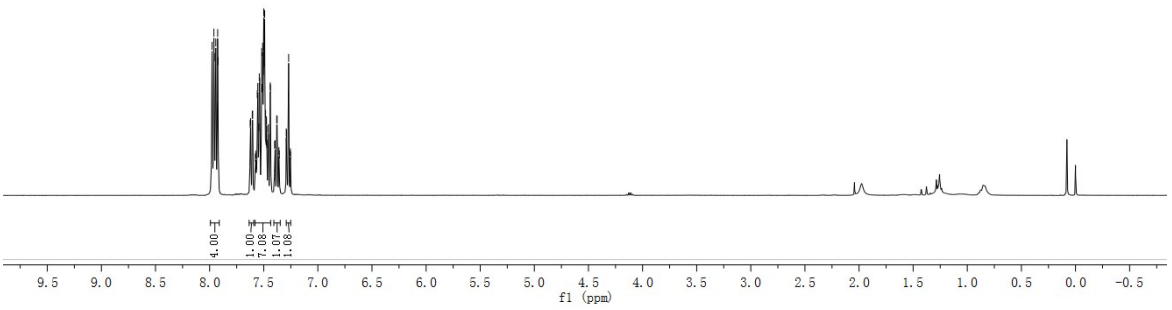
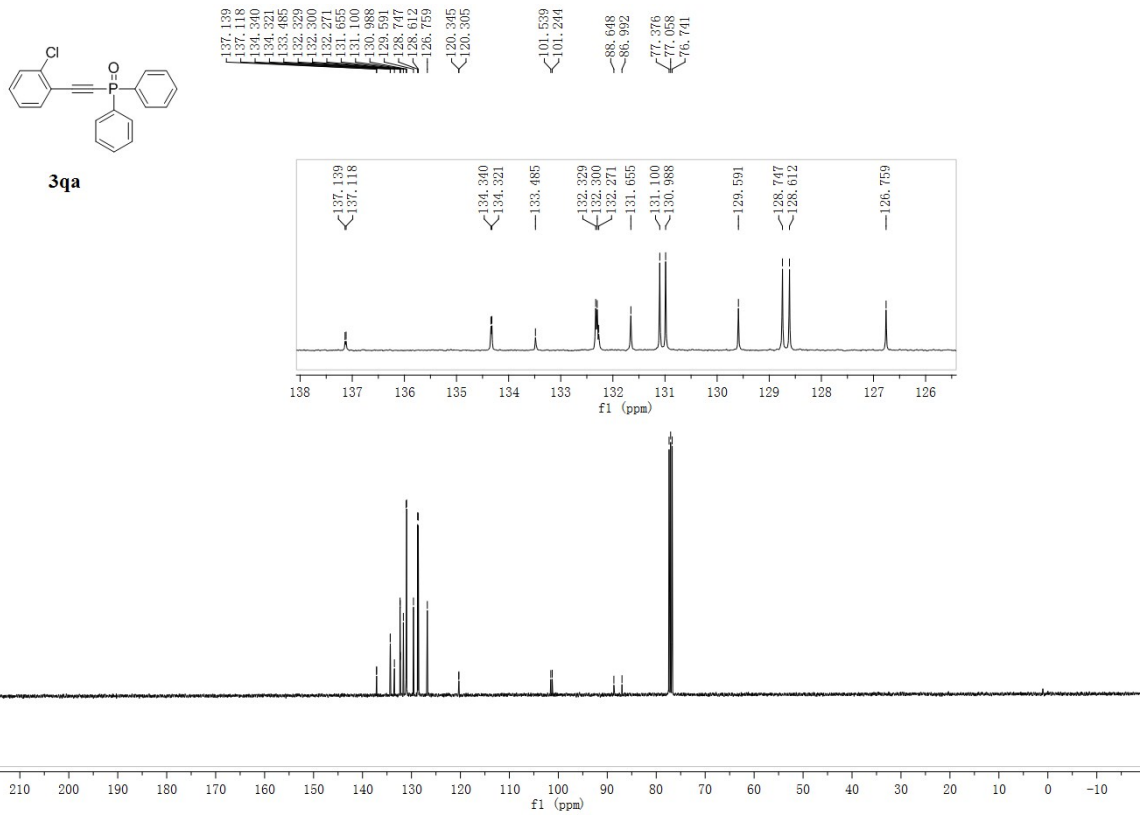
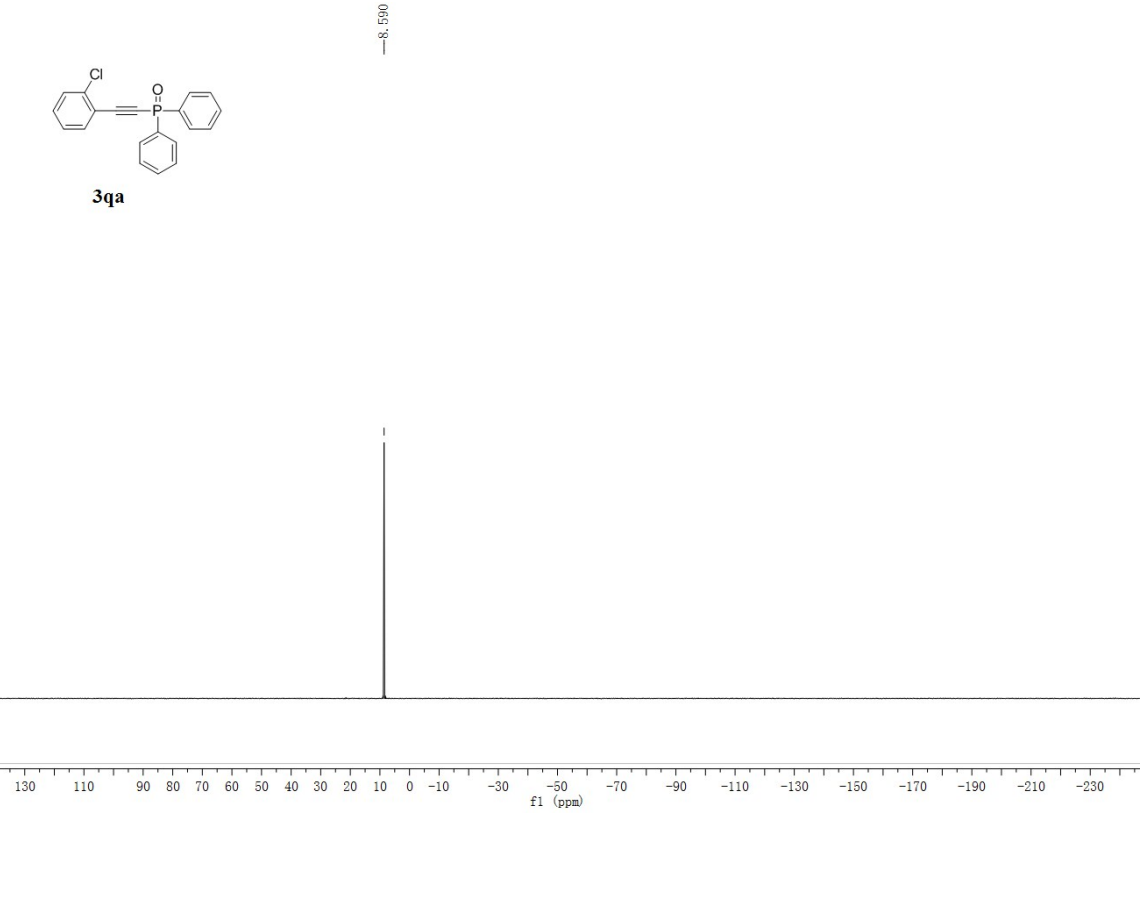
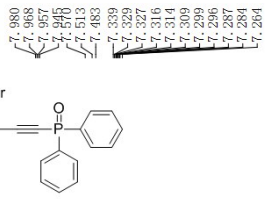

7.978
7.961
7.957
7.943
7.926
7.922
7.625
7.622
7.606
7.602
7.549
7.537
7.511
7.496
7.479
7.460
7.438
7.395
7.376
7.356
7.292
7.289
7.273
7.270
7.254
7.252
4.00
1.00
7.08
1.07
1.08
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)

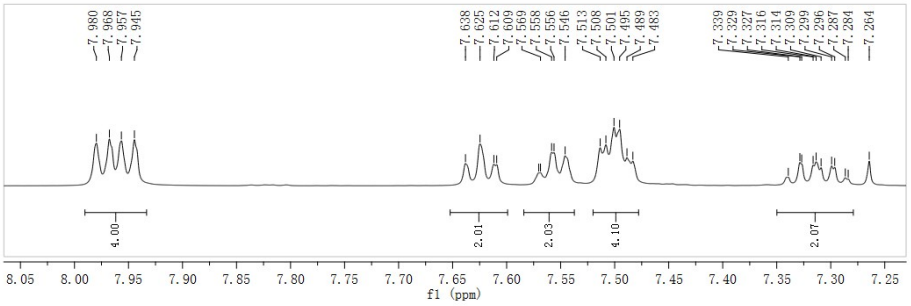

4.00
1.00
7.08
1.07
1.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

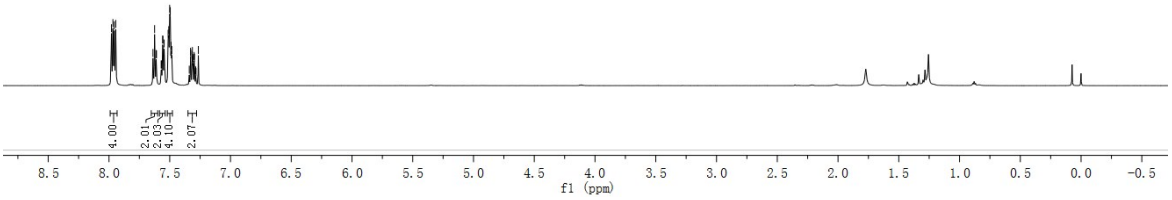

137.139
137.118
134.340
134.321
133.485
132.329
132.300
132.271
131.655
131.100
130.988
129.591
128.747
128.612
126.759
120.345
120.305
101.539
101.244
88.648
86.992
77.376
77.058
76.741
Cl
O
P
3qa
f1 (ppm)

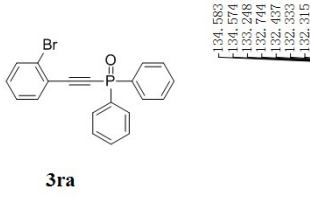

8.590
Cl
O
P
3qa
f1 (ppm)



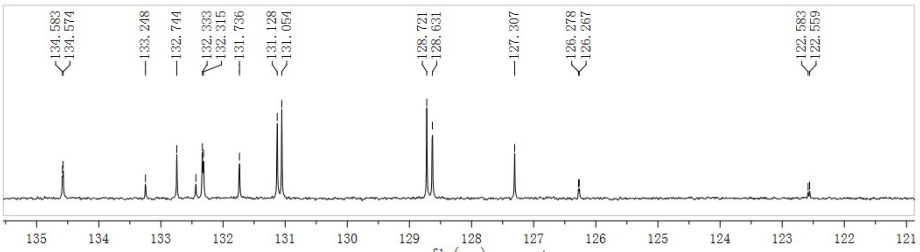
3ra

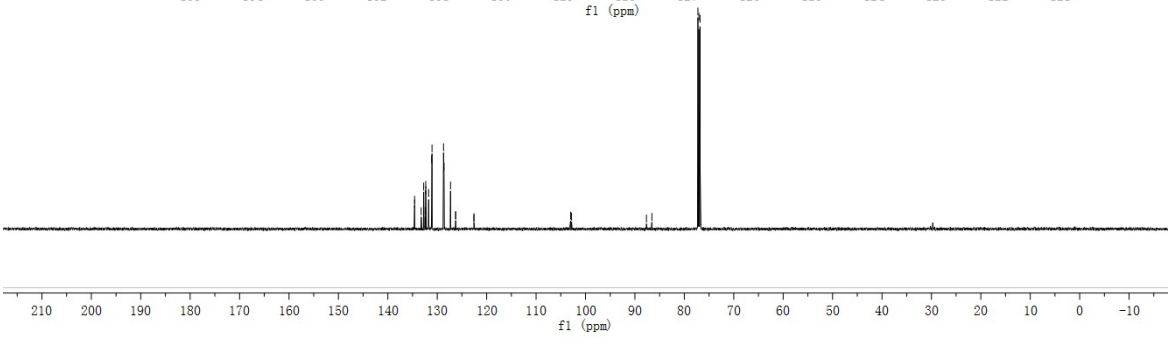


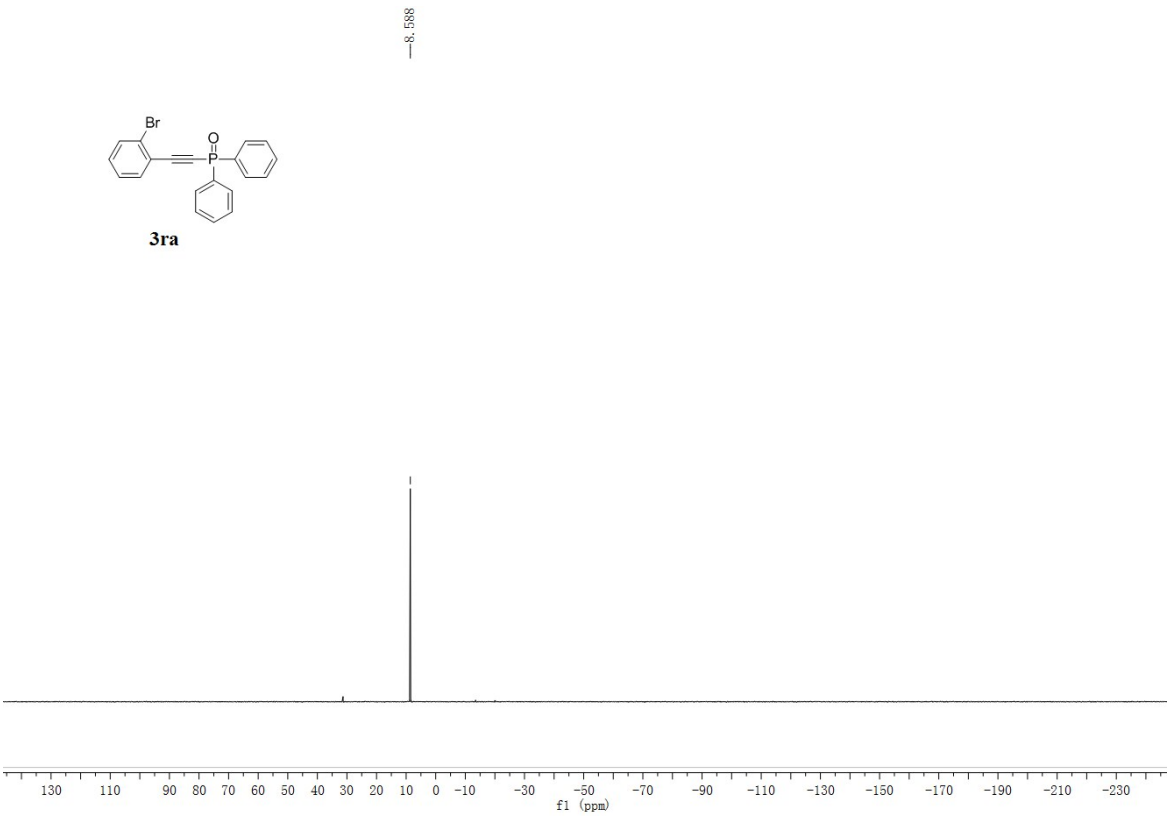


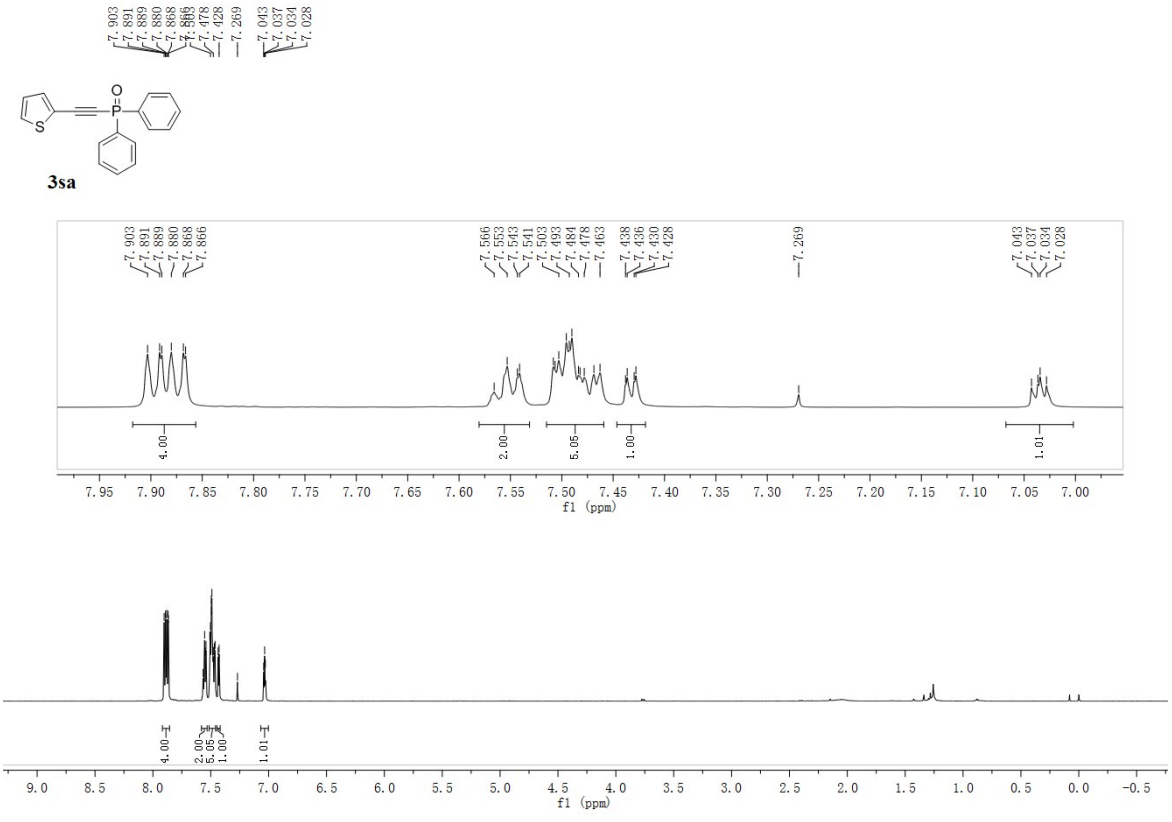


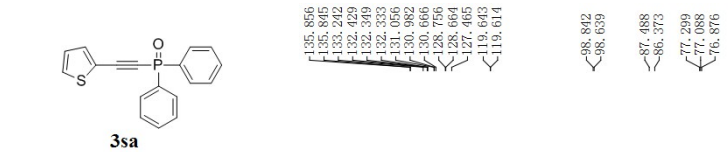
3ra



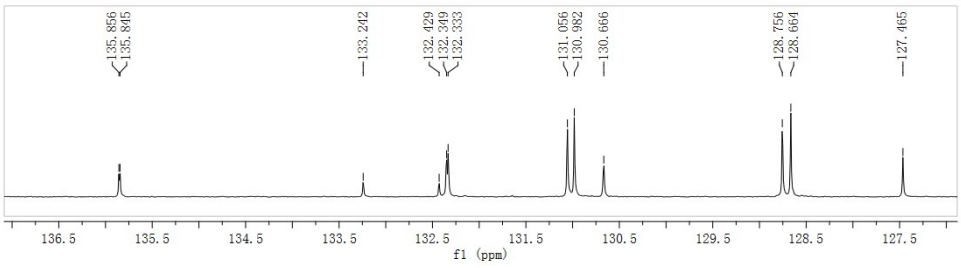


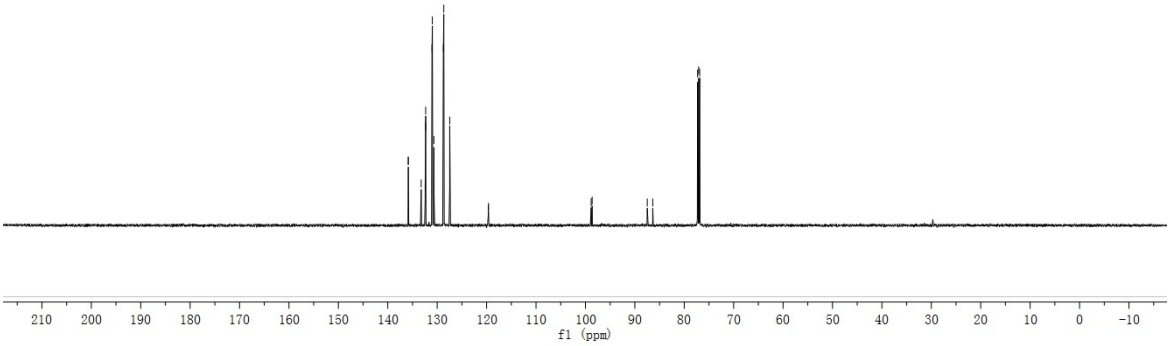

8.588
Br
O
P
3ra
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


7.903
7.891
7.889
7.880
7.868
7.866
7.566
7.553
7.543
7.541
7.503
7.493
7.484
7.478
7.463
7.438
7.436
7.430
7.428
7.269
7.043
7.037
7.034
7.028
O
P
S
3sa
4.00
2.00
5.05
1.00
1.01
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

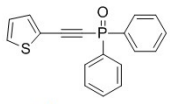

135.856
135.845
133.242
132.429
132.349
132.333
131.056
130.982
130.666
128.756
128.664
127.465
119.643
119.614
98.842
98.639
87.488
86.373
77.299
77.088
76.876

3sa

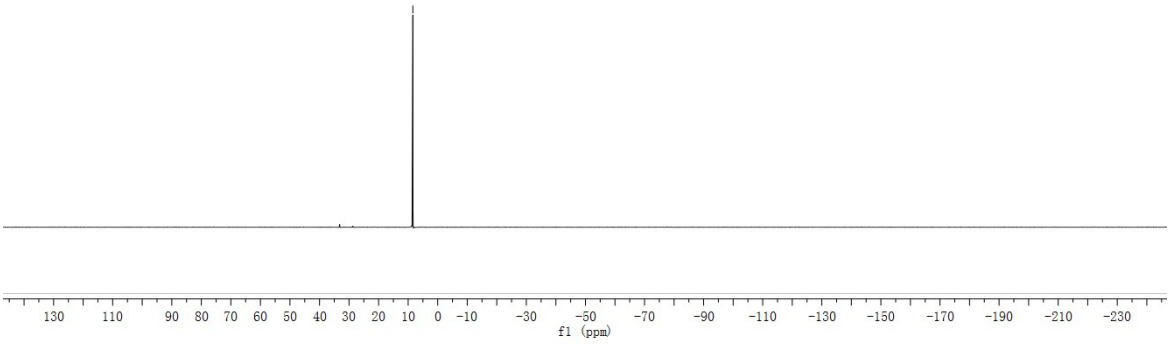

135.856
135.845
133.242
132.429
132.349
132.333
131.056
130.982
130.666
128.756
128.664
127.465
136.5
135.5
134.5
133.5
132.5
131.5
130.5
129.5
128.5
127.5
f1 (ppm)

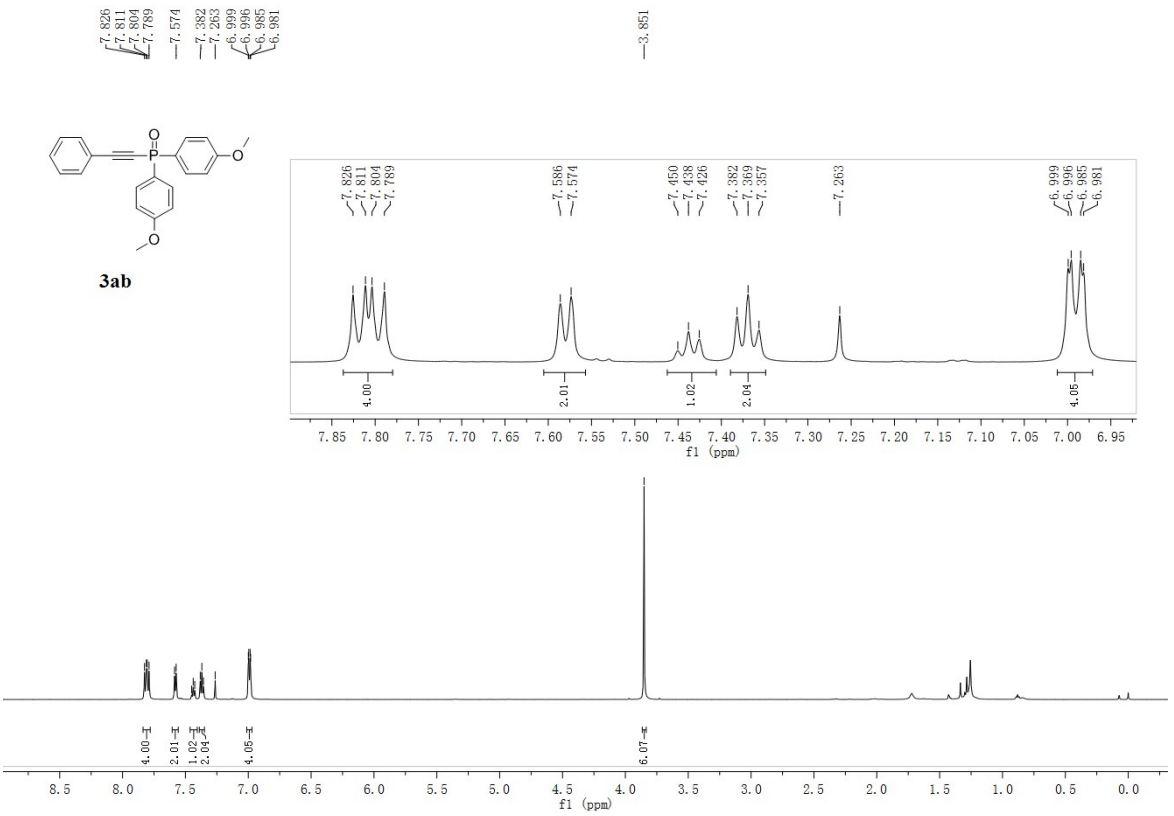

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

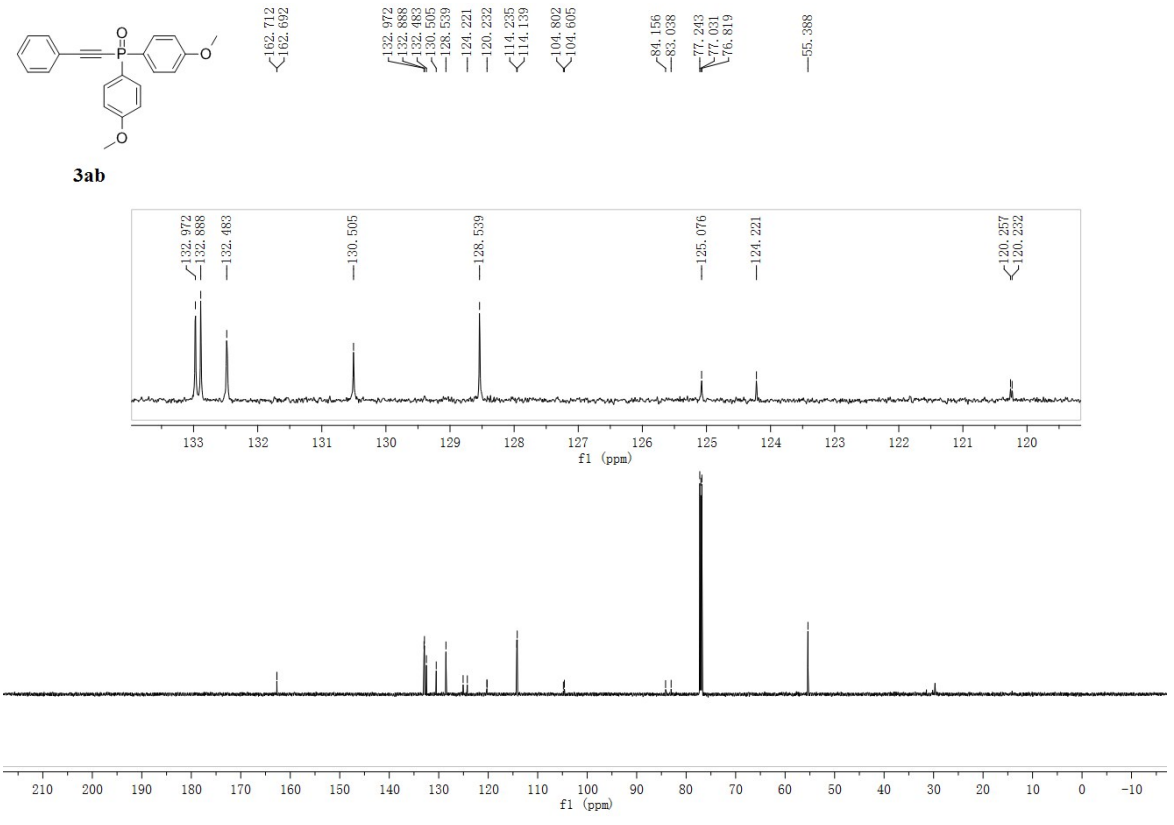

8.396

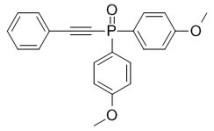


3sa


130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

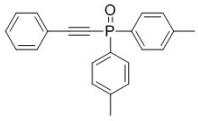

7.826
7.811
7.804
7.789
7.574
7.382
7.263
6.999
6.996
6.985
6.981
3.851
3ab
7.586
7.574
7.450
7.438
7.426
7.369
7.357
4.00
2.01
1.02
2.04
4.05
6.07
f1 (ppm)


162.712
162.692
132.972
132.888
132.483
130.505
128.539
124.221
120.232
114.235
114.139
104.802
104.605
84.156
83.038
77.243
77.031
76.819
55.388
3ab
125.076
120.257
120.232
f1 (ppm)



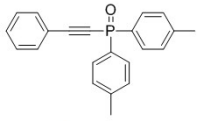
3ab

8.108
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



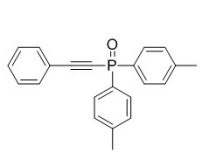
3ac

7.805
7.785
7.771
7.751
7.588
7.570
7.567
7.451
7.432
7.414
7.379
7.360
7.342
7.302
7.296
7.283
7.276
7.268
2.397
4.00
2.00
1.02
2.05
4.02
6.01
f1 (ppm)



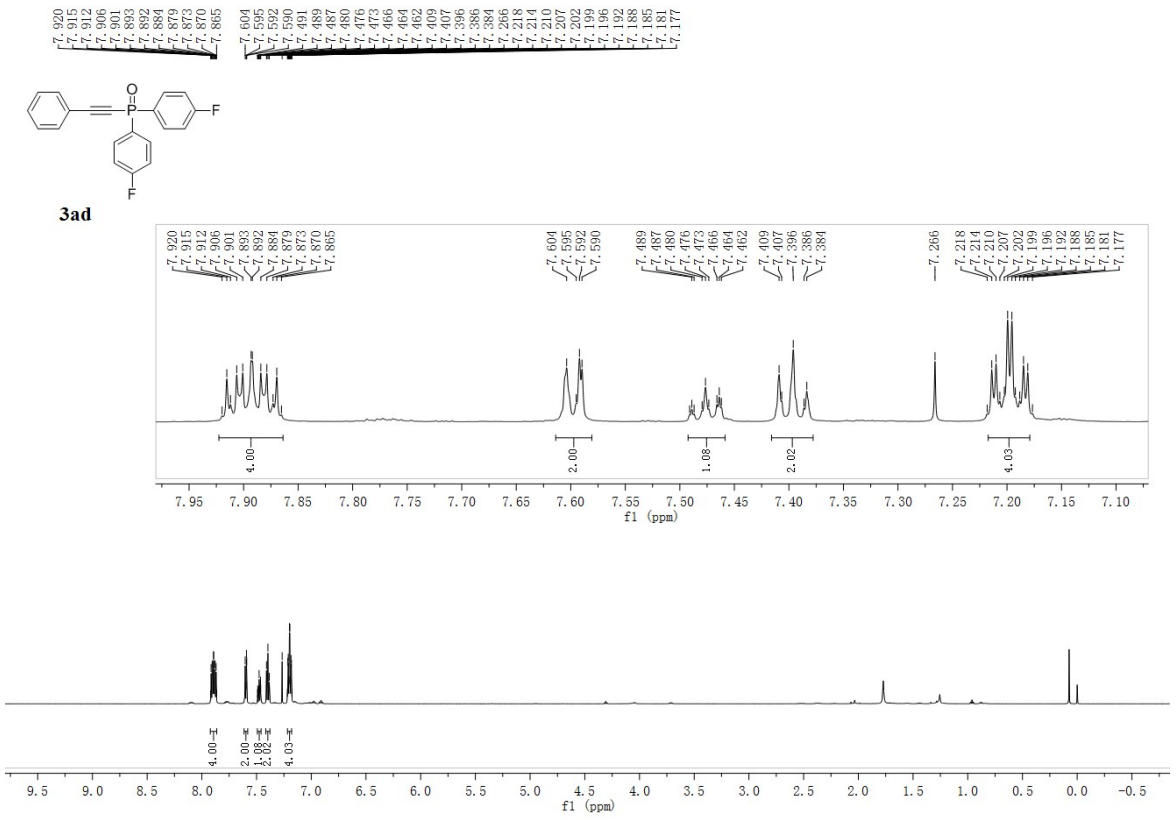
3ac

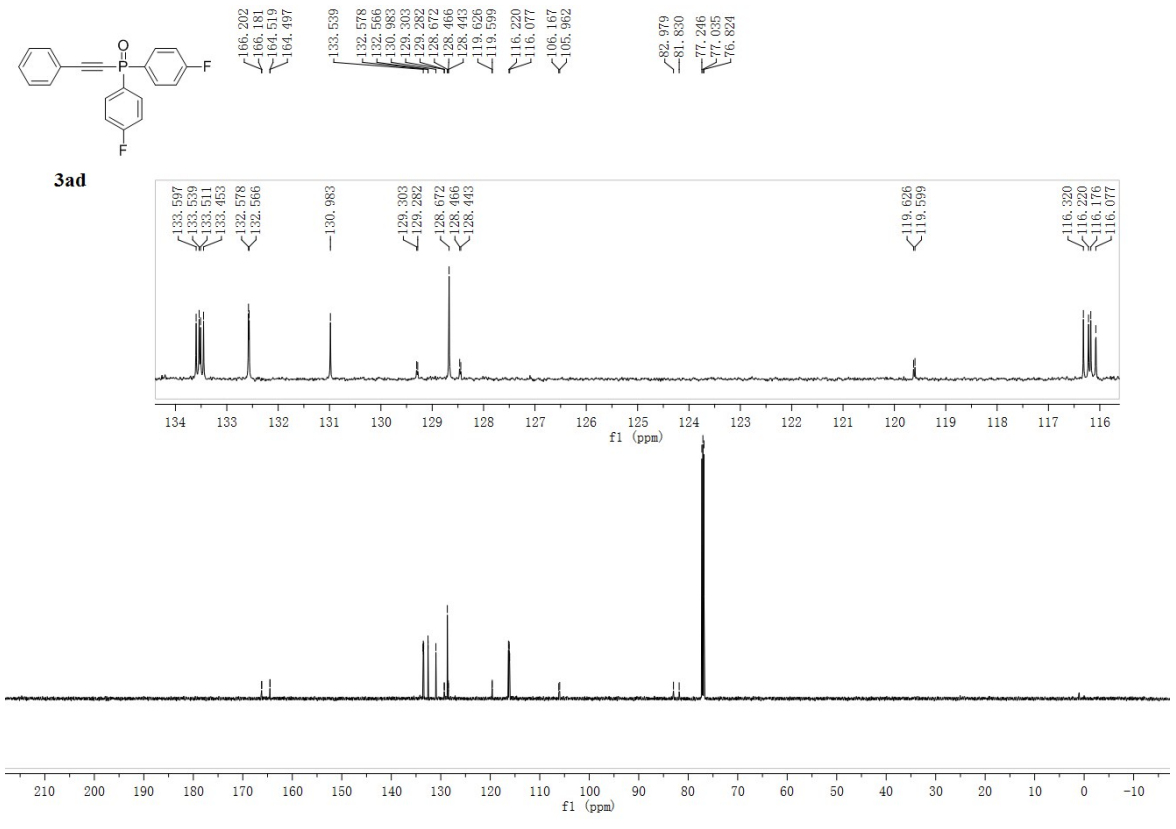
142.756
142.728
130.951
130.561
129.443
129.304
128.544
120.184
120.144
105.043
104.747
84.207
82.527
77.404
77.086
76.768
21.649
132.499
132.481
131.066
130.951
130.680
130.561
129.443
129.304
128.544
f1 (ppm)
f1 (ppm)

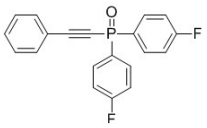


3ac

8.672
f1 (ppm)

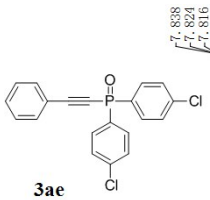

3ad
f1 (ppm)


3ad
f1 (ppm)

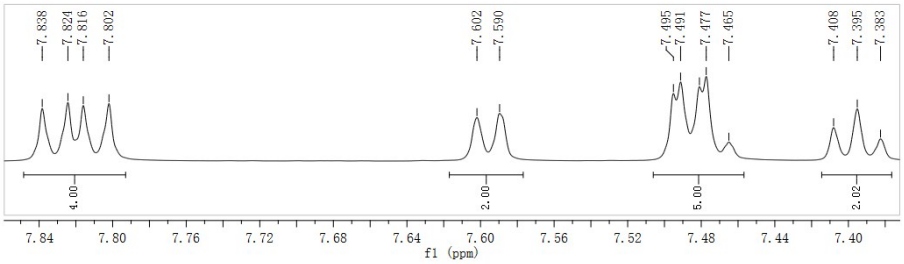


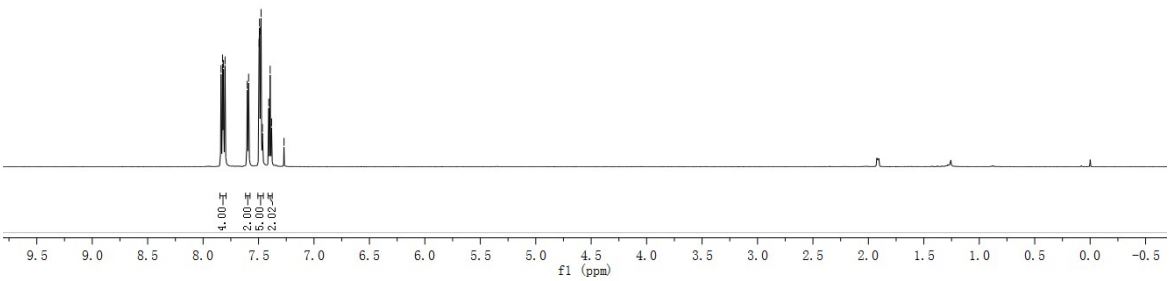
3ad

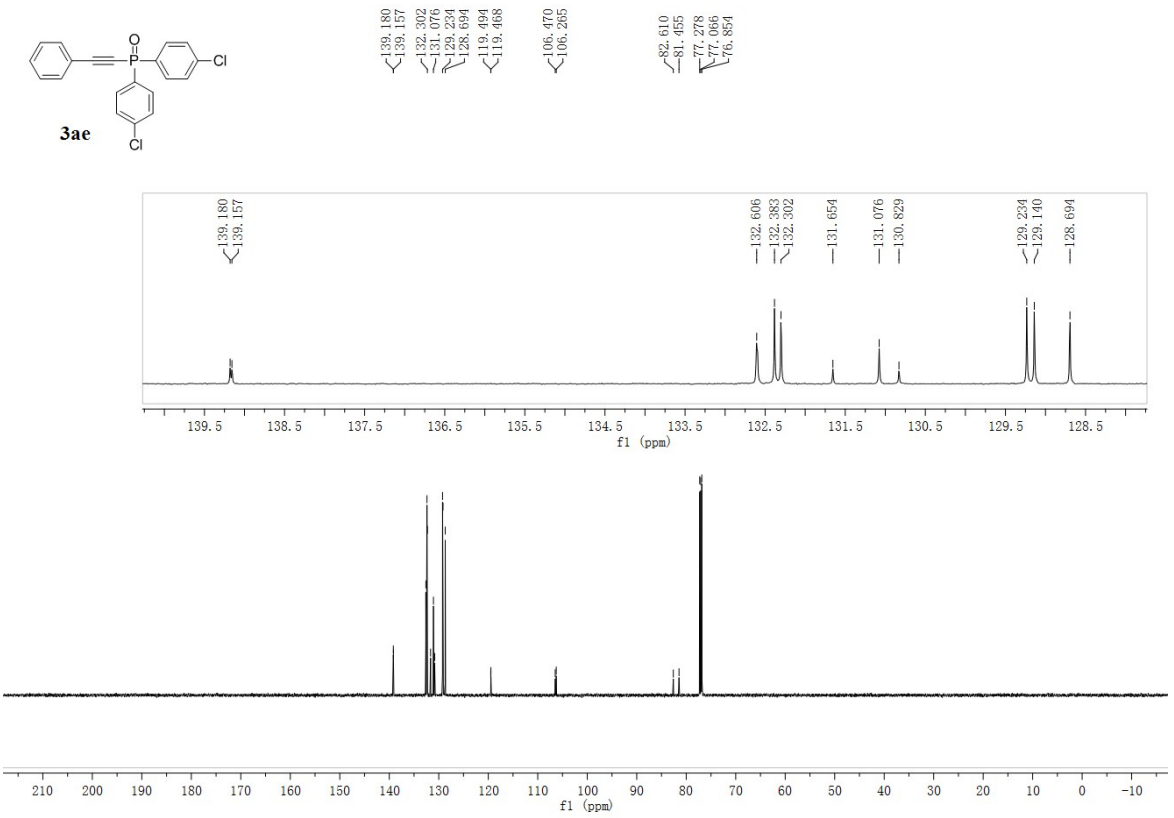
6.198
f1 (ppm)

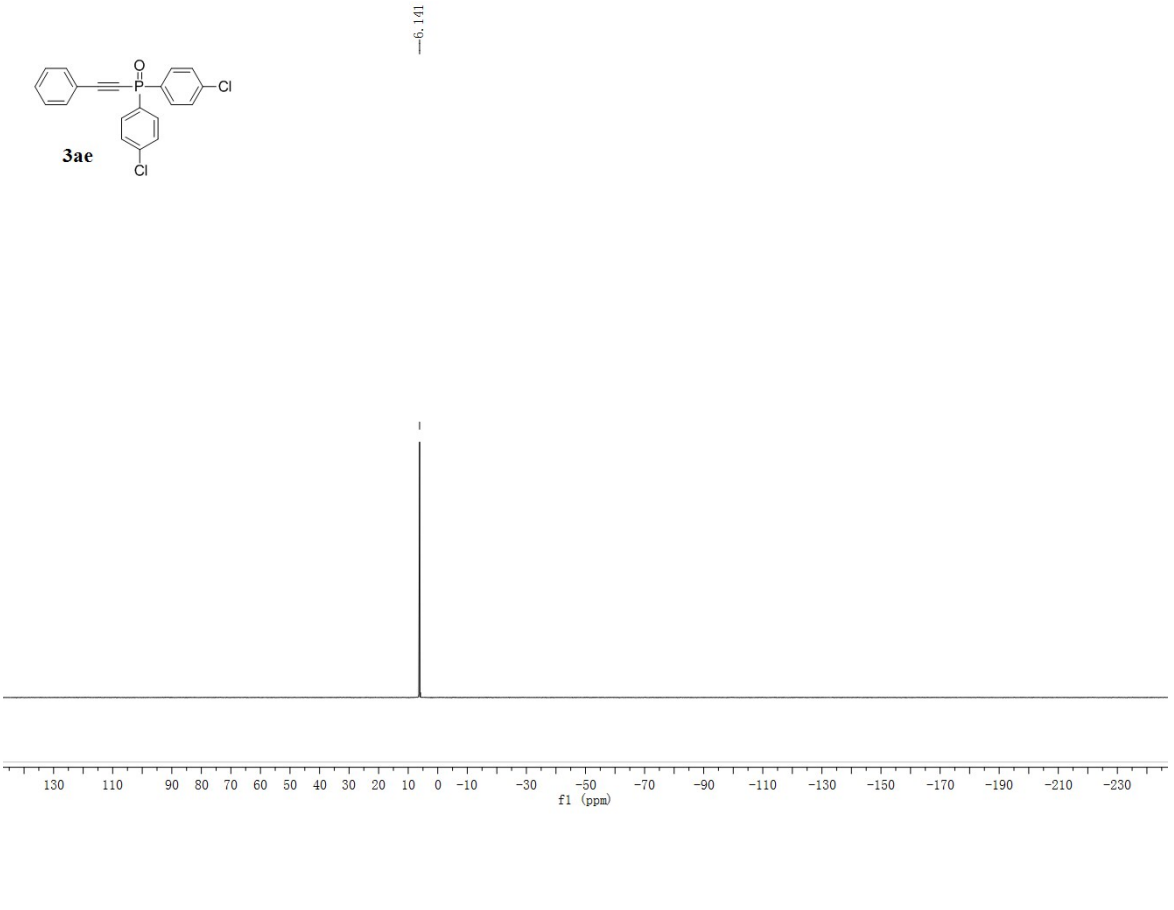


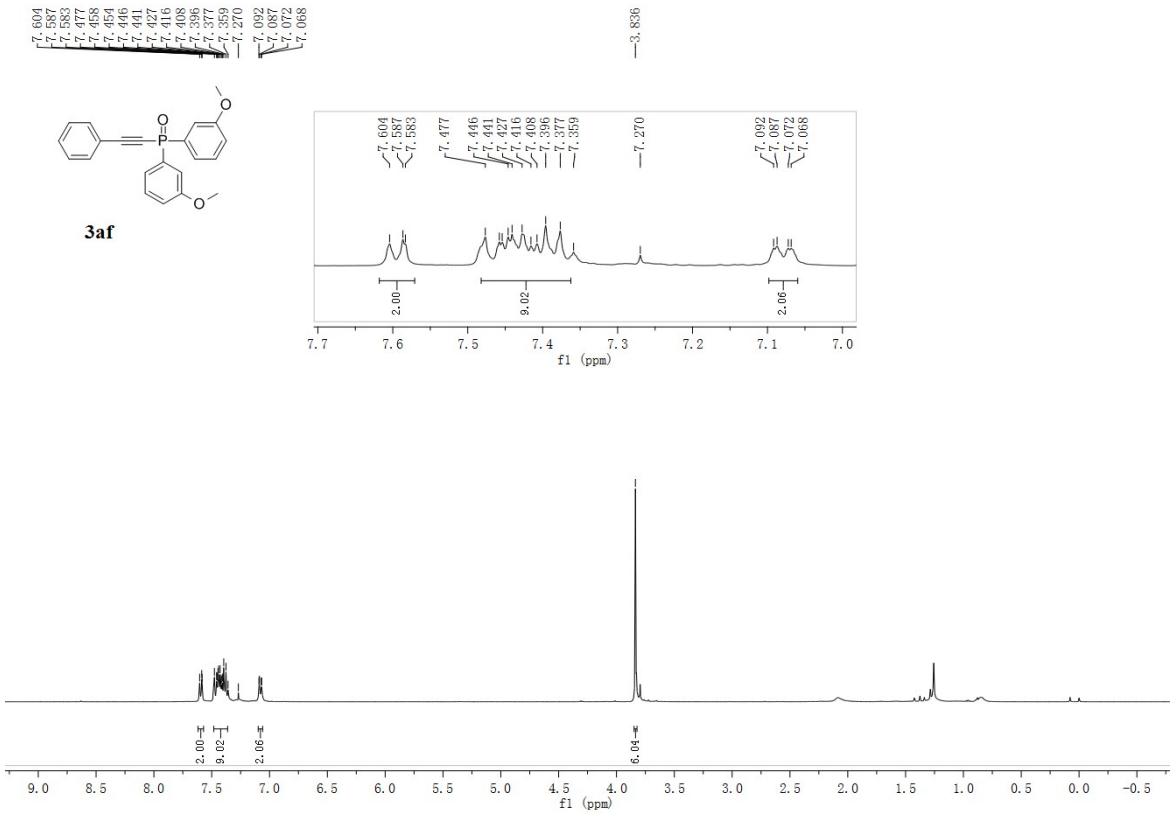
3ae

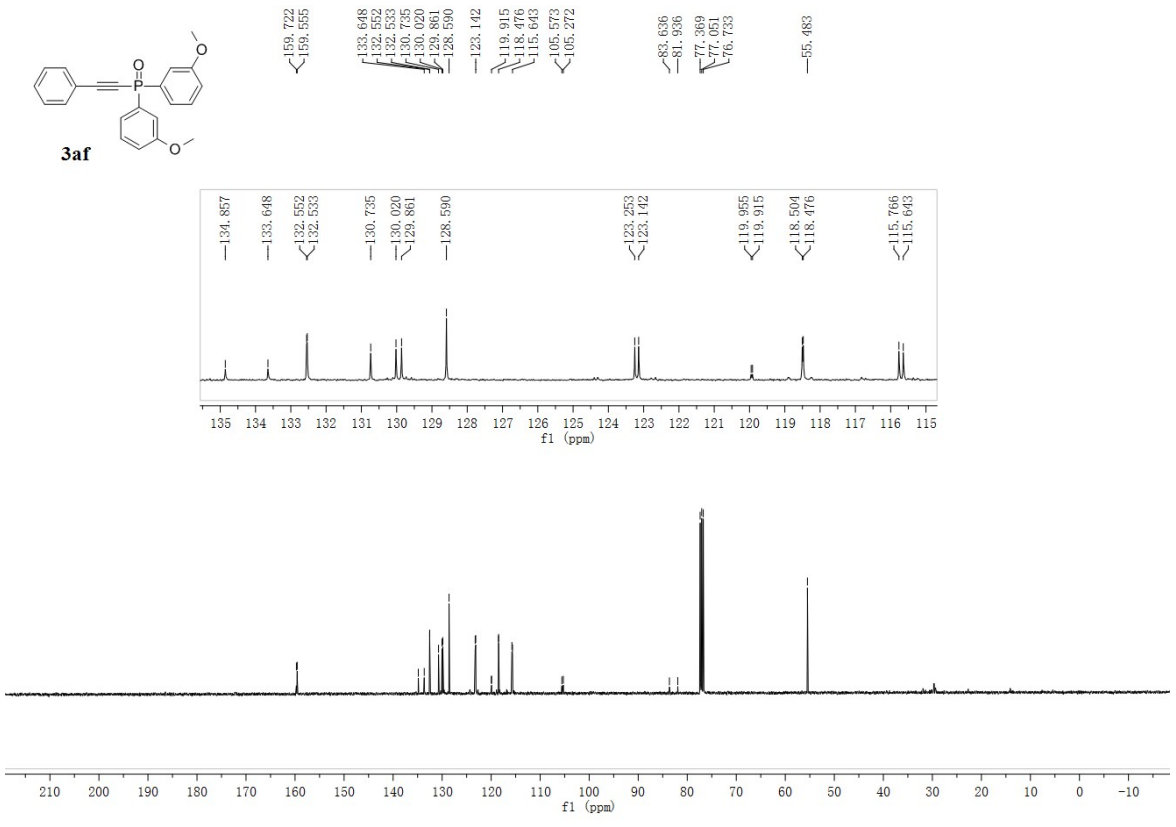

7.838
7.824
7.816
7.802
7.602
7.590
7.495
7.491
7.477
7.465
7.408
7.395
7.383
4.00
2.00
5.00
2.02
f1 (ppm)

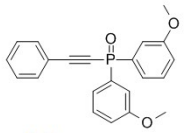

4.00
2.00
5.00
2.02
f1 (ppm)


3ae
Cl
Cl
139.180
139.157
132.302
131.076
129.234
128.694
119.494
119.468
106.470
106.265
82.610
81.455
77.278
77.066
76.854
f1 (ppm)
f1 (ppm)


3ae
Cl
Cl
6.141
f1 (ppm)

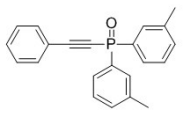

7.604
7.587
7.583
7.477
7.458
7.454
7.446
7.441
7.427
7.416
7.408
7.396
7.377
7.359
7.270
7.092
7.087
7.072
7.068
3.836
3af
2.00
9.02
2.06
6.04
f1 (ppm)


159.722
159.555
133.648
132.552
132.533
130.735
130.020
129.861
128.590
123.142
119.915
118.476
115.643
105.573
105.272
83.636
81.936
77.369
77.051
76.733
55.483
3af
134.857
133.648
132.552
132.533
130.735
130.020
129.861
128.590
123.253
123.142
119.955
119.915
118.504
118.476
115.766
115.643
f1 (ppm)



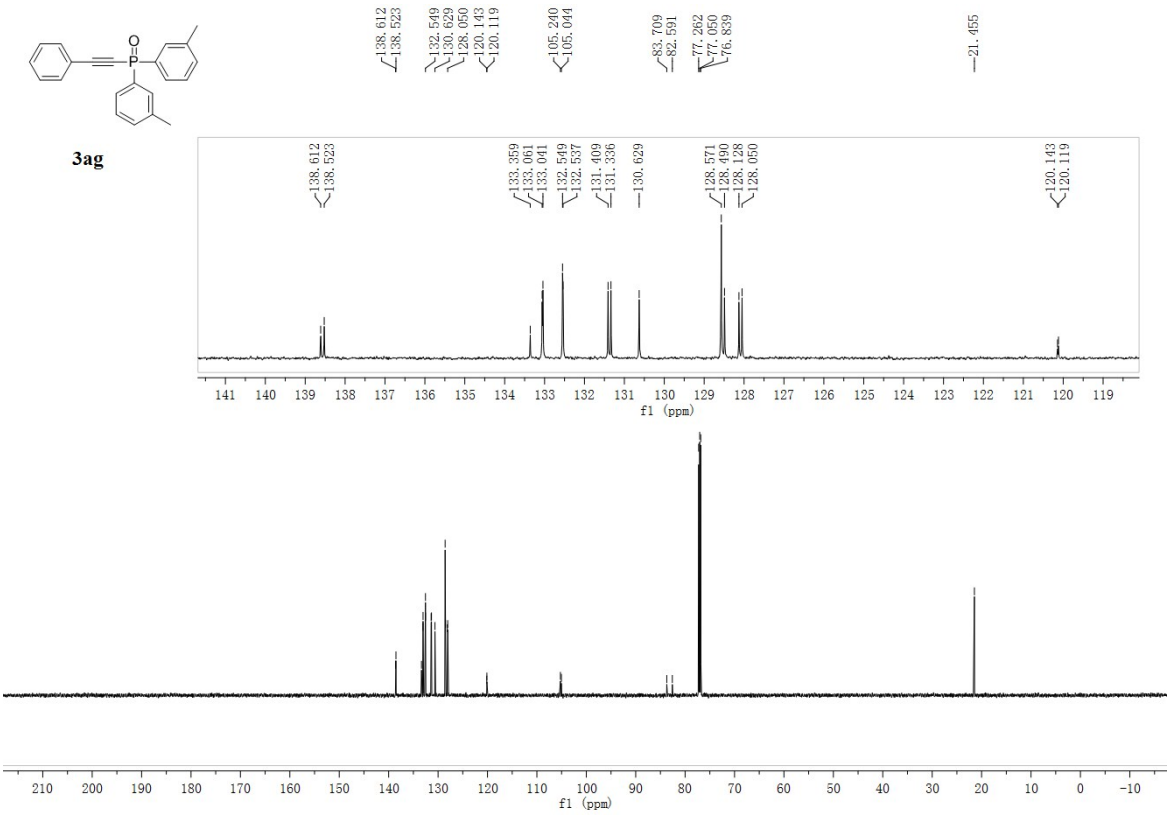
3af

8.382
f1 (ppm)



3ag

7.744
7.721
7.694
7.682
7.671
7.659
7.605
7.596
7.593
7.591
7.460
7.451
7.448
7.444
7.437
7.435
7.433
7.391
7.388
7.380
7.378
7.375
7.368
7.365
7.361
7.358
7.347
7.263
2.399
2.00
2.01
2.05
1.00
6.07
6.03
f1 (ppm)


3ag
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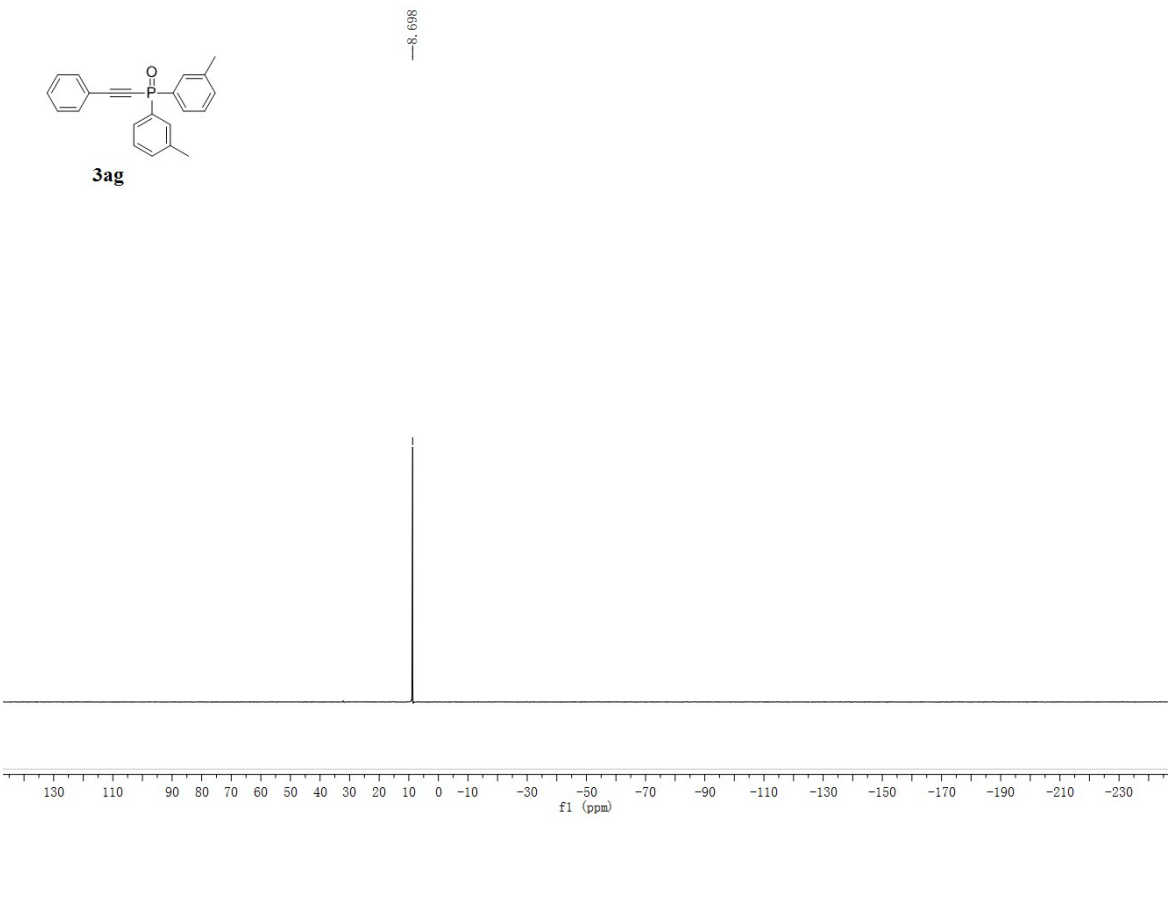
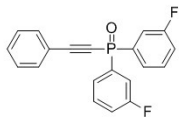
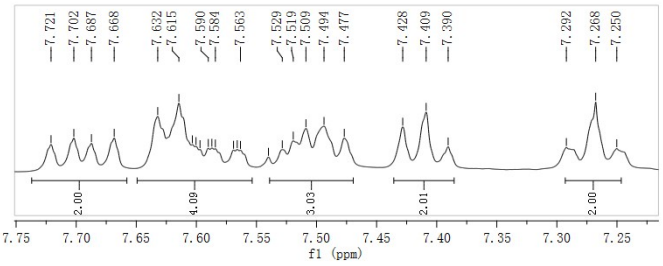
138.523
132.549
130.629
128.060
120.143
120.119
105.240
105.044
83.709
82.591
77.262
77.050
76.839
21.455
133.359
133.061
133.041
132.549
132.537
131.409
131.336
130.629
128.571
128.490
128.128
128.050
f1 (ppm)

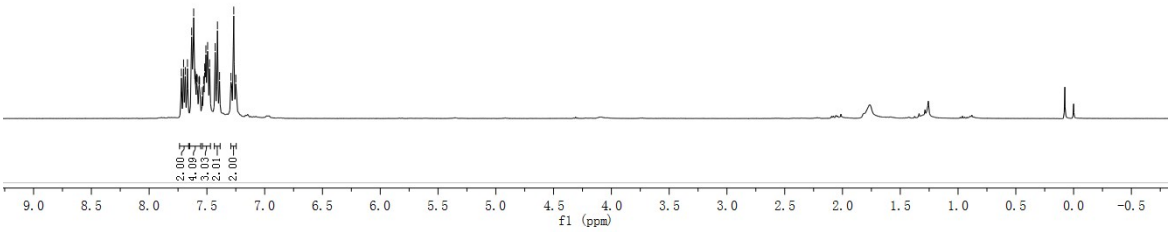

8.698
3ag
f1 (ppm)

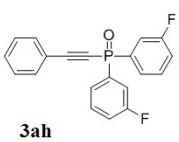

7.721
7.702
7.687
7.668
7.632
7.615
7.603
7.600
7.597
7.590
7.587
7.584
7.569
7.566
7.563
7.540
7.529
7.519
7.509
7.494
7.477
7.428
7.409
7.390
7.292
7.268
7.250


O
P
F
F

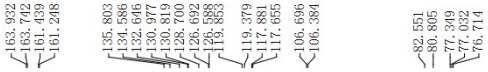
3ah


7.721
7.702
7.687
7.668
7.632
7.615
7.590
7.584
7.563
7.529
7.519
7.509
7.494
7.477
7.428
7.409
7.390
7.292
7.268
7.250
2.00
4.09
3.03
2.01
2.00
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)


2.00
4.09
3.03
2.01
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O
P
F
F

3ah


163.932
163.742
161.439
161.248
135.803
134.586
132.646
130.977
130.819
128.700
126.692
126.588
119.853
119.379
117.881
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106.696
106.384
82.551
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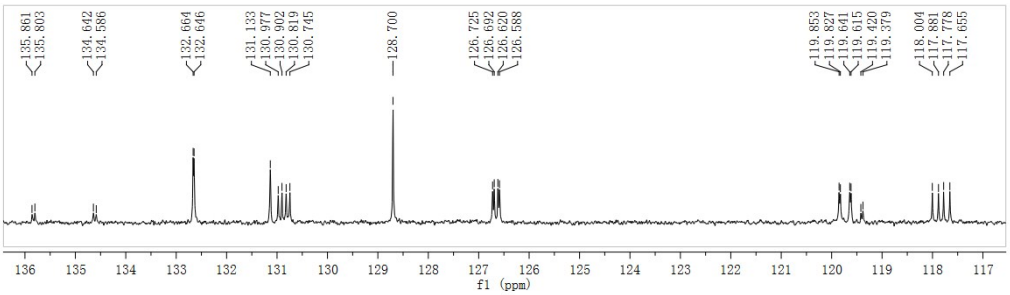
77.349
77.032
76.714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130.977
130.902
130.819
130.745
128.700
126.725
126.692
126.620
126.588
119.853
119.827
119.641
119.615
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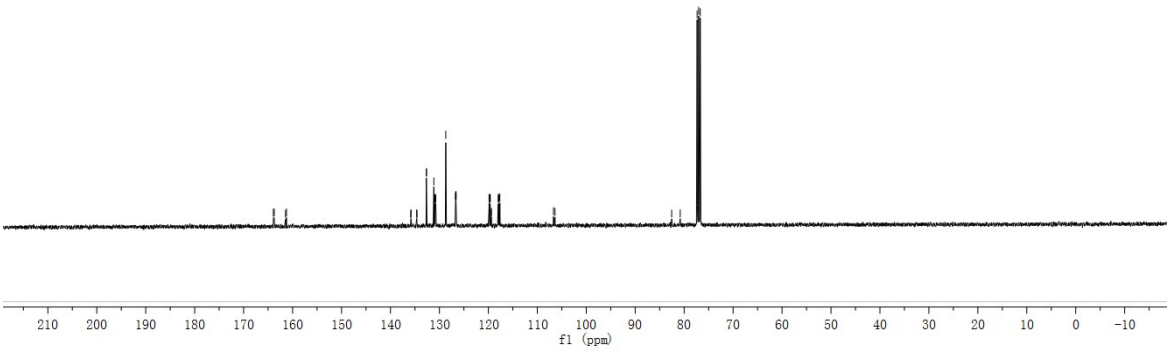
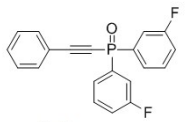
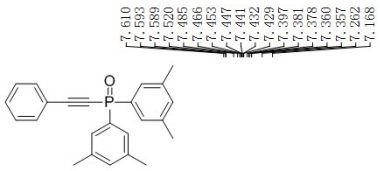
117.881
117.778
117.655
136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



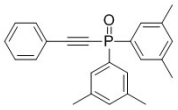
3ah

5.325
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



3ai

7.610
7.593
7.589
7.520
7.485
7.466
7.453
7.447
7.441
7.432
7.429
7.397
7.381
7.378
7.360
7.357
7.262
7.168
2.357
2.00
4.01
1.04
2.06
2.04
12.02
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



3ai

138.427
138.287
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128.568
128.458
120.282
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104.681
84.264
82.580
77.357
77.039
76.722
21.332
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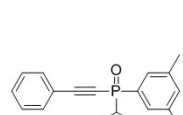
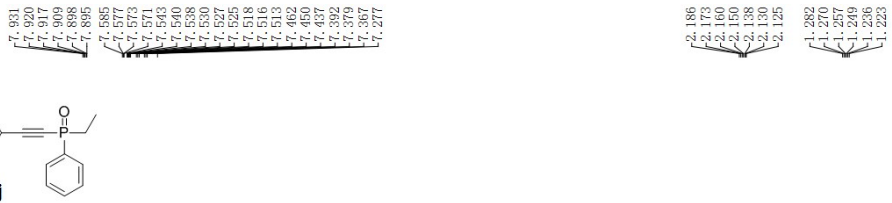
128.568
128.541
128.458
f1 (ppm)



3ai

9.124
f1 (ppm)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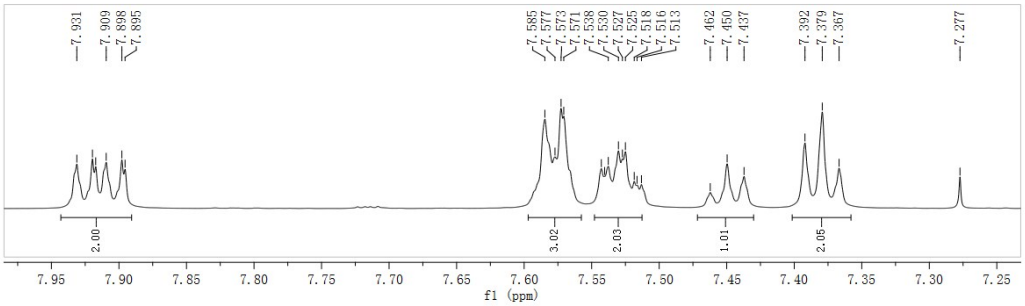
7.909
7.898
7.895
7.585
7.577
7.573
7.571
7.543
7.540
7.538
7.530
7.527
7.525
7.518
7.516
7.513
7.462
7.450
7.437
7.392
7.379
7.367
7.277
2.186
2.173
2.160
2.150
2.138
2.130
2.125
1.282
1.270
1.257
1.249
1.236
1.223

3aj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7.530
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7.525
7.518
7.516
7.513
7.462
7.450
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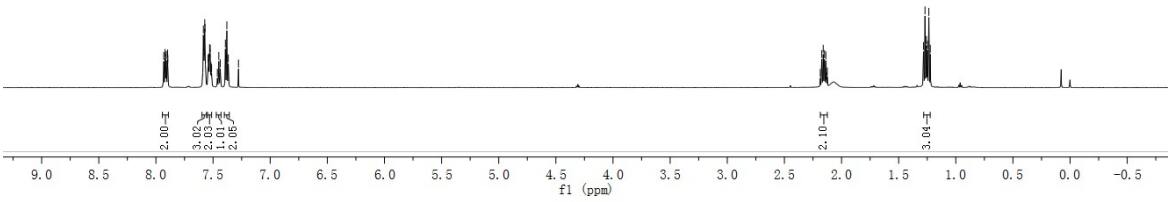
7.392
7.367
7.277
2.00
3.02
2.03
1.01
2.05
f1 (ppm)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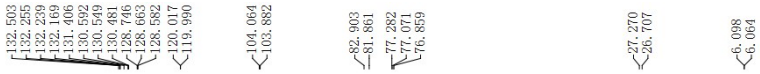
3.02
2.03
1.01
2.05
2.10
3.04
f1 (ppm)


132.503
132.255
132.239
132.169
131.406
130.592
130.549
130.481
128.746
128.663
128.582
120.017
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104.064
103.882
82.903
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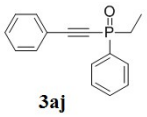
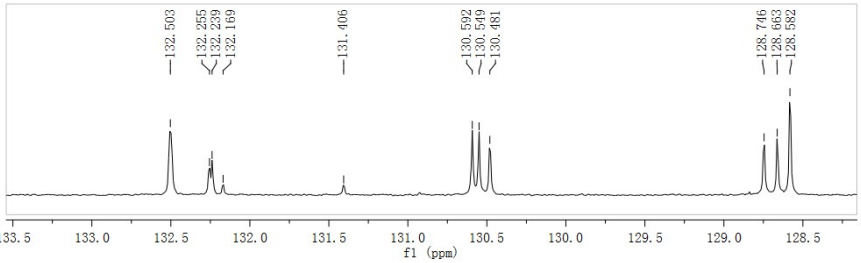
77.282
77.071
76.859
27.270
26.707
6.098
6.064



3aj


132.503
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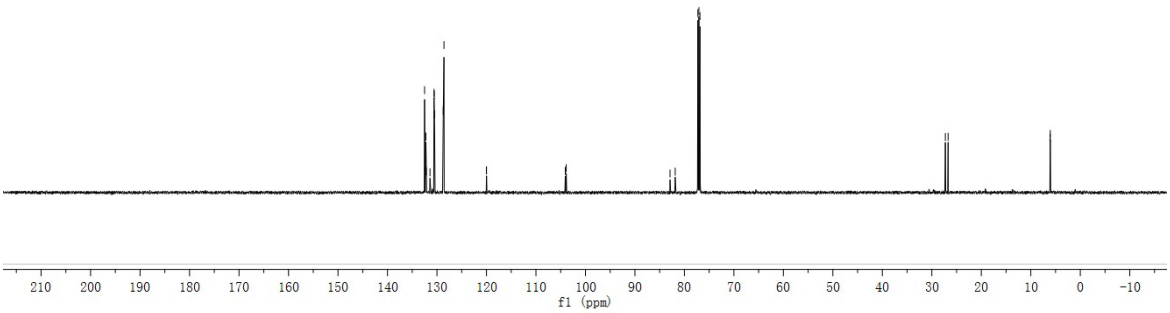
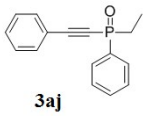
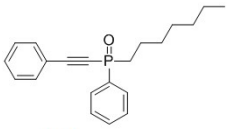
132.239
132.169
131.406
130.592
130.549
130.481
128.746
128.663
128.582
f1 (ppm)

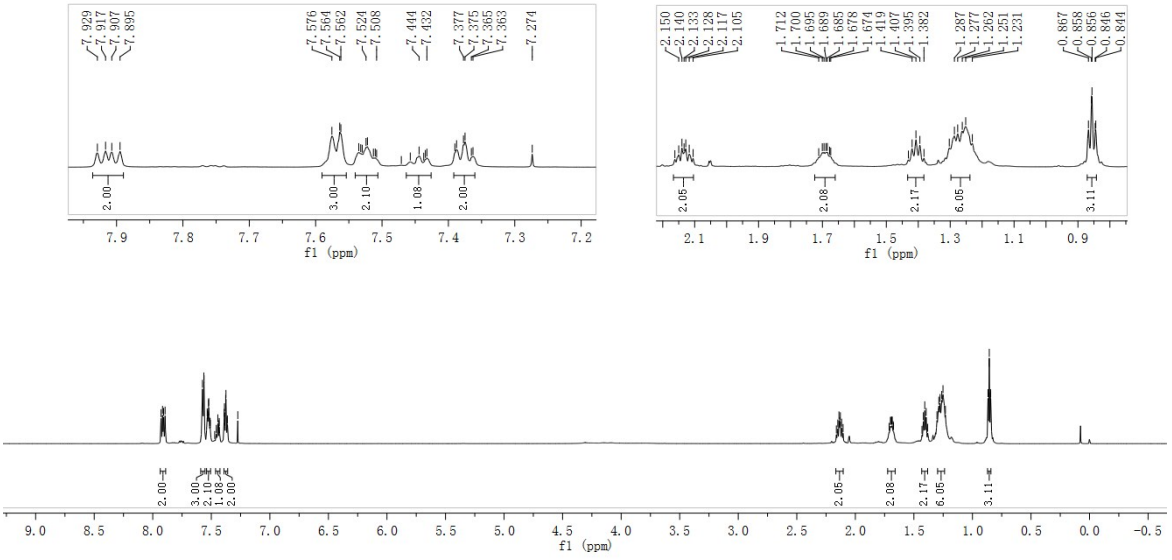

f1 (ppm)

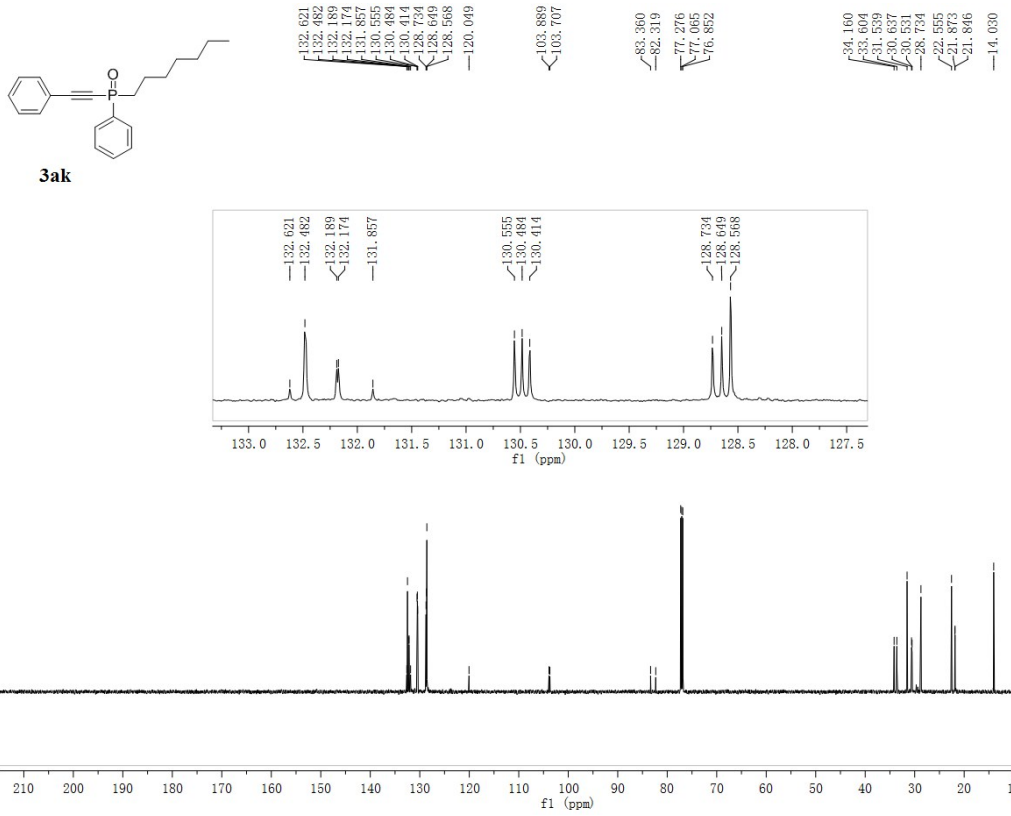


3aj



3ak

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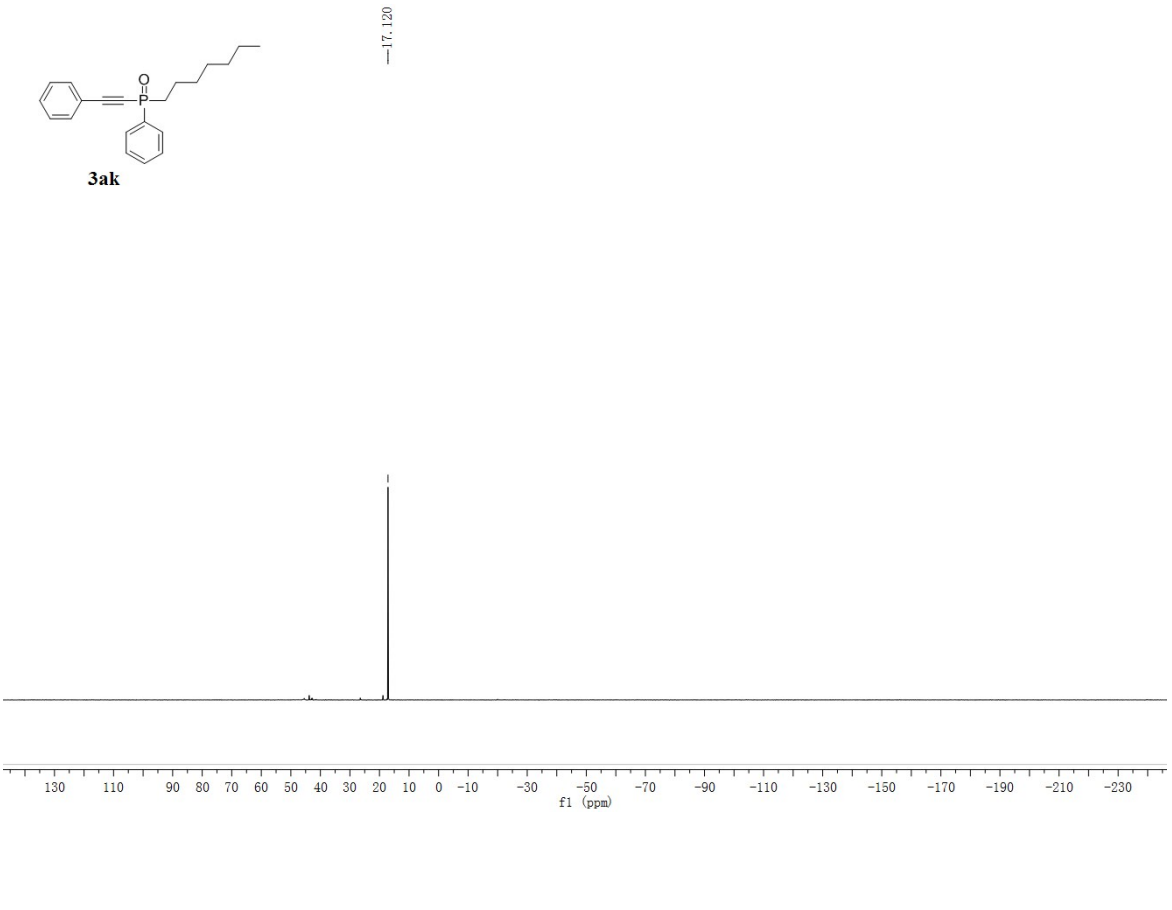
130.414
128.734
128.649
128.568
120.049
103.889
103.707
83.360
82.319
77.276
77.065
76.852
34.160
33.604
31.539
30.637
30.531
28.734
22.555
21.873
21.846
14.030
3ak
f1 (ppm)


17.120
3ak
f1 (ppm)